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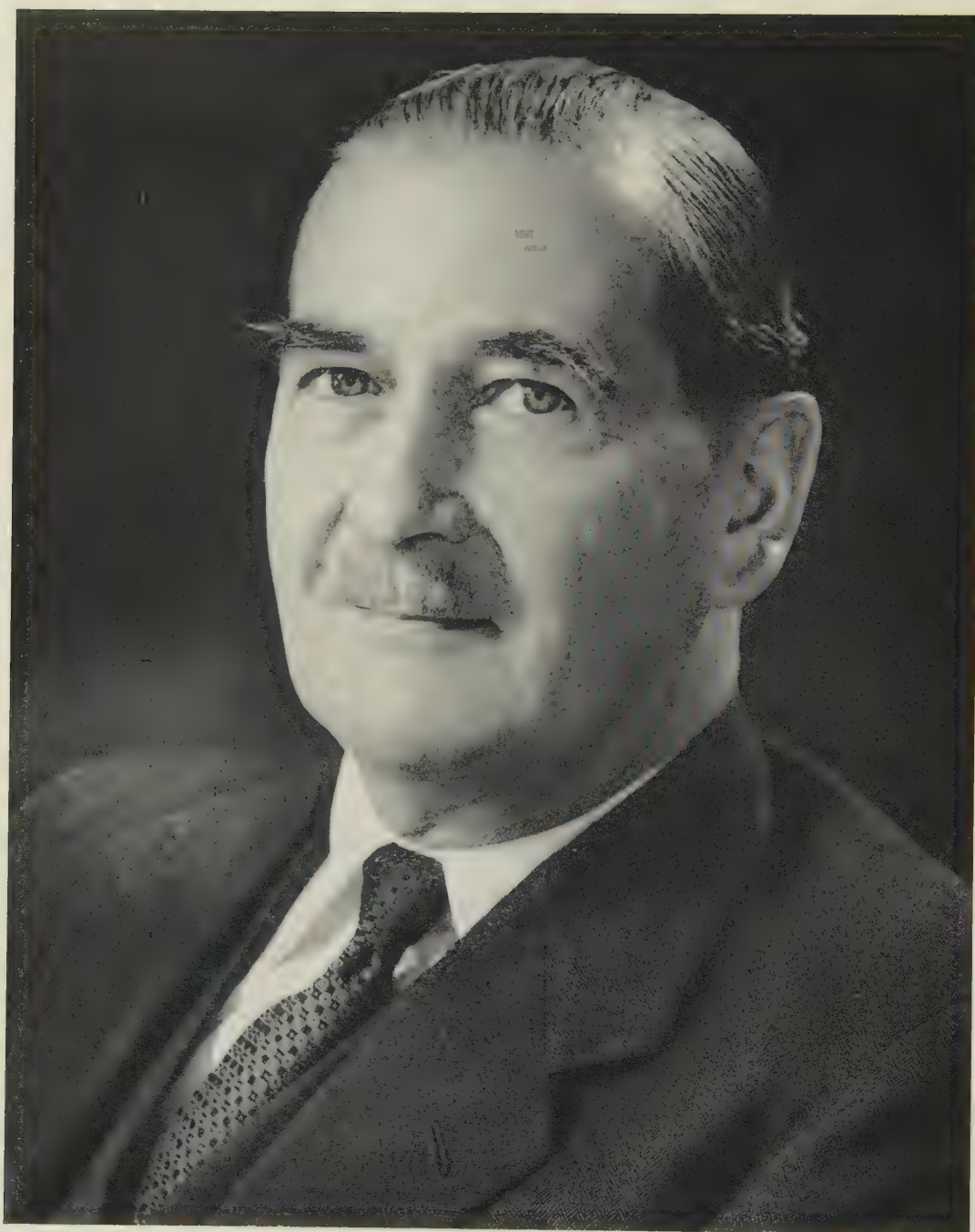
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† Paper contributed to a Symposium on "The Metallurgy of Niobium".



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# THE INSTITUTE OF METALS

## MINUTES OF PROCEEDINGS

### GENERAL MEETING

27 February 1957

A GENERAL MEETING of the Institute of Metals was held in the Chemistry Lecture Theatre, the University, Edgbaston, Birmingham, at 10.30 a.m. on Wednesday, 27 February 1957. The Chair was taken at the morning session by Professor E. C. ROLLASON, Ph.D., M.Sc., F.I.M. (Professor of Industrial Metallurgy, University of Birmingham) and at the afternoon session by Professor H. FORD, D.Sc., Ph.D., M.I.Mech.E. (Professor of Applied Mechanics, Imperial College of Science and Technology, and Chairman of the Metallurgical Engineering Committee).

#### INFORMAL DISCUSSION ON "DEGREASING"

An all-day Informal Discussion took place, to which numerous contributions were made, after an opening address by Mr. J. E. ENTWISTLE.

At the conclusion of the meeting, the Chairman proposed, and there were passed, votes of thanks to Mr. Entwistle for his opening address and to the University authorities for permitting the use of the Chemistry Lecture Theatre.

### ANNUAL SPRING MEETING

29 April to 7 May 1957

THE FORTY-NINTH ANNUAL SPRING MEETING of the Institute of Metals took the form of a Joint Meeting with the Associazione Italiana di Metallurgia, the Association Suisse pour l'Essai des Matériaux, and the Société Suisse des Constructeurs de Machines, held in London from Monday 29 April to Friday 3 May 1957 and in Provincial Centres on Sunday, Monday, and Tuesday, 5, 6, and 7 May.

Monday, 29 April

#### SCIENTIFIC SESSION OF THE ASSOCIAZIONE ITALIANA DI METALLURGIA

The meeting opened at 10.0 a.m. at Church House, Great Smith Street, Westminster, S.W.1, with a scientific session arranged by the Associazione Italiana di Metallurgia. The President of the Associazione, Dott. Aldo DACCÒ, took the Chair.

The following papers were presented and discussed in Italian:

"Recovery of Metallic Cadmium from Zinc-Smelter By-Products by Amalgam Metallurgy", by G. Binetti and A. Vaschetti.

"The Corrosion of Metals at Elevated Temperatures by Vanadium Pentoxide: Behaviour of Alloys Containing Titanium", by A. Burdese and S. Gallo.

"Research on Copper-Chromium-Silicon and Copper-Cobalt-Silicon Alloys of High Electrical Conductivity", by S. Gallo.

"The Influence of the Type of Cladding on the Corrosion-Resistance of Aluminium-Zinc-Magnesium-Copper (Ergal-Type) Alloys", by A. Prati, A. Gragnani, and D. Gualandi.

#### VISITS

Members of the Italian and Swiss societies paid visits, in the afternoon, to the laboratories of The British Non-

Ferrous Metals Research Association, London; the laboratories of The British Iron and Steel Research Association, London; the works and laboratories of High Duty Alloys, Ltd., Slough, and the precious-metal refinery and laboratories of The Mond Nickel Co., Ltd., Acton. The ladies made a coach tour of London.

#### OPENING CEREMONY

At the Royal Institution, Albemarle Street, London, W.1, at 6.30 p.m., the President, Major C. J. P. BALL, D.S.O., M.C., welcomed the delegates and ladies of the Associazione Italiana di Metallurgia, the Association Suisse pour l'Essai des Matériaux, and the Société Suisse des Constructeurs de Machines, on behalf of the Council and Members of the Institute of Metals.

Dott. Aldo DACCÒ (President) replied on behalf of the Associazione Italiana di Metallurgia, and Professor Dr. A. von ZEERLEDER, (President, Association Suisse pour l'Essai des Matériaux), on behalf of the two Swiss societies.

#### FORTY-SEVENTH MAY LECTURE

Sir ERIC ASHBY, D.Sc., Sc.D., LL.D., D.I.C., President and Vice-Chancellor of The Queen's University of Belfast, then delivered the Forty-Seventh Annual May Lecture on "Technological Humanism".

At the conclusion of the lecture, Professor C. W. DANNATT, A.R.S.M., D.I.C., proposed a vote of thanks to Sir Eric Ashby for his lecture, which is printed on pp. 461-467 of this volume of the *Journal*.

After the lecture, the Council gave a dinner party at the Army and Navy Club, Pall Mall, London, S.W.1, at which the Presidents and Members of Council of the Italian and Swiss societies, the May Lecturer, and other distinguished delegates to the meeting were the guests of the Institute.

Tuesday, 30 April

#### ANNUAL GENERAL MEETING

THE FORTY-NINTH ANNUAL GENERAL MEETING of the Institute of Metals was held at Church House, Great Smith Street, London, S.W.1, at 9.30 a.m. The retiring President, Major C. J. P. BALL, D.S.O., M.C., occupied the Chair at the opening of the meeting.

The minutes of the last General Meetings held in Germany on 16-25 September 1956; in London on 3 and 4 December 1956, and in Birmingham on 27 February 1957, were taken as read and signed by the Chairman.

#### Elections of Members

The Secretary (Lieut.-Colonel S. C. GUILLAN, T.D.) announced that since the Autumn Meeting held in Germany on 16-25 September 1956, a total of 322 members had been elected on 17 October, 14 November, 5 December, and 31 December 1956, and on 8 February, 6 March, and 26 April 1957, the lists of whose names are printed in the *Bulletin* 1956-57, vol. 3, pp. 133, 141, 148, 159, 165, and 177.

#### Report of Council for the Year Ended 31 December 1956

The Chairman moved, Dr. IVOR JENKINS (Vice-President) seconded, and there was carried unanimously a motion for the adoption of the Report of Council for the year ended 31 December 1956, which is published on pp. 345-356 of this volume of the *Journal*.

*Report of the Honorary Treasurer and Accounts for the  
Financial Year Ended 30 June 1956*

The Honorary Treasurer, Mr. J. C. COLQUHOUN, M.B.E., moved, Mr. R. D. HAMER, B.Sc., F.I.M. (Chairman of the Finance and General Purposes Committee) seconded, and there was carried unanimously a motion for the adoption of the Report of the Honorary Treasurer and accounts for the financial year ended 30 June 1956. The report and accounts are published in this volume of the *Journal*, pp. 357-360.

*Re-Election of Auditors*

A motion for the re-election of the auditors, Messrs. Poppleton and Appleby, was proposed, by Mr. R. LEMMY, seconded by Mr. T. Henry TURNER, M.Sc., M.I.Mech.E., F.I.M., and carried unanimously.

*Election of Officers for 1957-58*

The Secretary announced that the following members had been elected to fill vacancies on the Council for the year 1957-58:

*President:*

L. B. PFEIL, O.B.E., D.Sc., A.R.S.M., F.I.M., F.R.S.

*Vice-Presidents:*

The Hon. JOHN GRIMSTON, M.P.  
Marshal of the Royal Air Force The Right Hon. The  
Lord TEDDER, G.C.B., D.C.L., Hon.LL.D.

*Ordinary Members of Council:*

Professor J. W. CUTHBERTSON, D.Sc., F.I.M.  
Sir RONALD PRAIN, O.B.E.  
F. WAINE, J.P.

*Senior Vice-President for 1957-58*

The Secretary announced that the Council had elected Marshal of the Royal Air Force the Right Hon. the Lord TEDDER, G.C.B., D.C.L., Hon.LL.D., to serve as Senior Vice-President for 1957-58.

*Vote of Thanks to Retiring Officers*

Professor J. W. CUTHBERTSON, D.Sc., F.I.M. (Member of Council), proposed, and there was carried with acclamation, a vote of thanks to the following retiring officers for their services on the Council: Professor F. C. Thompson, D.Met., M.Sc., F.I.M., Past-President; Major P. Litherland Teed, A.R.S.M., F.R.Ae.S., M.I.M., F.I.M., Vice-President; and Dr. W. A. Baker, F.I.M., and Mr. E. R. Gadd, F.I.M., Ordinary Members of Council.

*Induction of New President*

The President, Major C. J. P. BALL, D.S.O., M.C., then introduced the new President, Dr. L. B. PFEIL, O.B.E., A.R.S.M., F.I.M., F.R.S., invested him with the Presidential Badge, and inducted him into the Chair.

*Vote of Thanks to Retiring President*

Mr. E. A. G. LIDDIARD, M.A., F.I.M., proposed, Professor H. O'NEILL, M.Met., D.Sc. (Member of Council) seconded, and there was carried with acclamation a hearty vote of thanks to the retiring President, Major C. J. P. BALL, D.S.O., M.C., for his services to the Institute. Major Ball briefly replied.

*Presidential Address*

Dr. L. B. PFEIL, O.B.E., A.R.S.M., F.I.M., F.R.S., then delivered his Presidential Address, which is published in this volume of the *Journal*, 457-461.

A vote of thanks to the President for his Address was proposed by Major P. Litherland TEED, A.R.S.M., and carried with acclamation.

*Institute of Metals (Platinum) Medal*

The President announced that the Council had awarded the Institute of Metals (Platinum) Medal for 1957 to Dr. Maurice COOK, Past-President, in recognition of his outstanding contributions to the science of metallurgy, to the non-ferrous metals industry, and to the welfare of the metallurgical profession. He said that as Dr. Cook was on his way to Australia, it was proposed to present the medal to him at the Autumn Meeting.

*Rosenhain Medal*

The President presented the Rosenhain Medal for 1957 to Dr. H. K. HARDY, A.R.S.M., A.I.M., Research Manager, United Kingdom Atomic Energy Authority, Industrial Group, Preston, in recognition of his outstanding contributions to knowledge in the field of physical metallurgy.

*W. H. A. Robertson Medal and Premium*

The President presented to Mr. E. GRIFFIN, A.M.I.Mech.E., A.M.I.Prod.E., Chief Engineer, Metal Sections, Ltd., Oldbury, the W. H. A. Robertson Medal and Premium of Fifty Guineas for 1956, awarded to him for his paper on "Cold Roll-Forming and Manipulation of Light-Gauge Sections", published in the *Journal*, 1955-56, Vol. 84, pp. 181-197.

The Annual General Meeting then concluded.

*COCKTAIL PARTY*

A cocktail party was held at noon, at Church House, Great Smith Street, London, S.W.1, to enable members to meet the Presidents, delegates, and ladies of the Italian and Swiss societies.

*VISITS*

During the morning delegates and ladies of the Italian and Swiss societies had paid a visit to Westminster Abbey.

During the afternoon the delegates visited the Research Laboratories of The British Aluminium Co., Ltd., Gerrards Cross; the Fraser and Chalmers Engineering Works of The General Electric Co., Ltd., Erith; the works of Frederick Braby and Co., Ltd., Crayford; and the works of the Telegraph Construction and Maintenance Co., Ltd., and Submarine Cables, Ltd., Greenwich.

*DISCUSSION ON "THE METAL PHYSICS OF CORROSION  
AND OXIDATION"*

At the resumed meeting at 2.30 p.m., at Church House, Great Smith Street, S.W.1, London, there was a discussion on "The Metal Physics of Corrosion and Oxidation", arranged by the Metal Physics Committee. The Chair was taken by Dr. T. P. HOAR, M.A., B.Sc., F.R.I.C., F.I.M. The discussion was opened by Dr. O. KUBASCHEWSKI and Dr. C. EDELEANU.

*RECEPTION BY THE SWISS MINISTER*

In the evening, a reception was held by His Excellency The Swiss Minister at his residence, 21 Bryanston Square, London, W.1, for Swiss visitors and Members of Council and their ladies.

*Wednesday, 1 May*

At the resumed meeting, at 9.30 a.m., at Church House, Great Smith Street, London, S.W.1, two concurrent scientific sessions were held; (i) an all-day Symposium on "Metal-



lurgical Aspects of the Control of Quality in Non-Ferrous Castings", arranged by the Metallurgical Engineering Committee in conjunction with the Institute of British Foundrymen, and (ii) discussions on the themes "The Metallurgy of Niobium" and "Liquid Metals".

#### SYMPOSIUM ON "METALLURGICAL ASPECTS OF THE CONTROL OF QUALITY IN NON-FERROUS CASTINGS"

At the morning session, the Chair was taken by the President, Dr. L. B. PFEIL, O.B.E., A.R.S.M., F.I.M., F.R.S.

Dr. W. A. BAKER, B.Sc., F.I.M., as Rapporteur, introduced the following eight invited papers, which had previously been published in the *Journal*.

At the afternoon session, the Chair was taken by Mr. H. J. V. WILLIAMS, President of the Institute of British Foundrymen.

There was an all-day discussion, a report of which is printed on pp. 518-534 of this volume of the *Journal*.

"The Metallurgical Principles of the Control of Quality of Non-Ferrous Castings", by R. W. Ruddell, M.A., F.I.M., and A. Cibula, M.A., A.I.M.

"The Role of Statistical Methods in Controlling the Quality of Non-Ferrous Castings", by A. R. Martin, B.Sc., A.R.S.M.

"Metallurgical Control of Quality in the Production of Aluminium Alloy Castings", by A. V. Carless, A.I.M.

"The Metallurgical Control of Quality in the Production of Copper-Base Alloy Castings", by A. R. French, F.I.M.

"The Control of Quality of Magnesium-Base Alloy Castings", by E. F. Emley, B.Sc., Ph.D., F.R.I.C., F.I.M., and P. A. Fisher, A.C.T., A.I.M.

"The Control of Quality in the Production of Nickel Alloy Sand Castings", by D. R. Wood, M.A., A.I.M., and J. F. Gregg, B.Sc.

"The Control of Quality of Pressure Die-Castings", by H. J. Sharp, M.Sc., A.I.M.

"Non-Destructive Testing in the Control of Quality of Non-Ferrous Castings", by S. L. Fry.

At the conclusion of the Symposium, votes of thanks to the authors and to the rapporteur were proposed by the Chairman and carried with acclamation.

#### DISCUSSION ON "THE METALLURGY OF NIOBIUM"

At the morning session, at 10.0 a.m., under the Chairmanship of Professor A. G. QUARRELL, D.Sc., Ph.D., A.R.C.S., D.I.C., F.Inst.P., F.I.M., a discussion, arranged by the Nuclear Energy Committee, was held, based on the following five papers, previously published in the *Journal*. The papers were presented by the individual authors. An account of the discussion appears on p. 547 of this volume of the *Journal*.

"The Development of Niobium", by A. B. McIntosh, Ph.D., B.Sc., A.R.C.S.T., F.R.I.C., F.I.M.

"The Melting Point of Niobium", by T. H. Schofield, M.Sc., F.I.M.

"The Physical and Mechanical Properties of Niobium", by C. R. Tottle, M.Met., A.I.M.

"Purification of Niobium by Sintering", by W. G. O'Driscoll, M.Sc., and G. L. Miller, Ph.D., B.Sc., A.R.I.C., M.I.M.M., M.I.Chem.E.

"The Production and Fabrication of Massive Niobium Metal", by L. R. Williams, B.Sc., F.I.M.

#### DISCUSSION ON "LIQUID METALS"

At the afternoon session, under the Chairmanship of Dr. H. M. FINNISTON, B.Sc., A.R.T.C., F.I.M. (Member of Council) a discussion was held on the theme "Liquid Metals", based on the following four papers, previously published

in the *Journal*. Dr. IVOR JENKINS, F.I.M., (Vice-President) introduced the papers, as Rapporteur.

"The Attack of Unstressed Metals by Liquid Mercury", by J. F. Strachan, B.Sc., A.M.I.E.E., A.Inst.P., and N. L. Harris, B.Sc., F.Inst.P.

"The Removal of Oxide from Aluminium by Brazing Fluxes", by M. F. Jordan, B.Sc., Ph.D., and D. R. Milner, M.Sc.

"Solution-Rate Studies with Liquid Metals: Solution of Copper in Liquid Lead and Bismuth", by A. G. Ward, L.I.M., and J. W. Taylor, Ph.D.

"Determination of the Surface Tensions of Molten Lead, Tin, and Indium by an Improved Capillary Method", by D. A. Melford, M.A., Ph.D., and T. P. Hoar, M.A., Ph.D., B.Sc., F.R.I.C., F.I.M.

At the conclusion of each session, votes of thanks to the authors and rapporteurs were proposed by the Chairmen and carried with acclamation.

#### VISIT

During the morning, delegates and ladies of the Italian and Swiss societies visited the National Gallery.

#### RECEPTION BY HER MAJESTY'S GOVERNMENT

In the evening, Her Majesty's Government held a reception at Lancaster House for delegates and ladies of the Italian and Swiss societies and representatives of British metallurgical science and industry.

#### Thursday, 2 May

At the resumed meeting at 10.0 a.m., at the Institute's Headquarters, 17 Belgrave Square, London, S.W.1, Dr. C. J. SMITHELLS, M.C., F.I.M. (Past-President) took the Chair at discussions on: (i) "Magnesium-Lithium Alloys", and (ii) "Effect of Composition on the Stress-Corrosion of Aluminium Alloys".

#### DISCUSSION ON "MAGNESIUM-LITHIUM ALLOYS"

The following three papers, previously published in the *Journal*, were introduced by Dr. E. F. EMLEY, B.Sc., F.R.I.C., F.I.M., who acted as Rapporteur:

"The Mechanical Properties of Binary and Ternary Magnesium Alloys Containing Lithium", by Professor W. R. D. Jones, D.Sc.

"Flow and Fracture Characteristics of Binary Wrought Magnesium-Lithium Alloys", by M. W. Toaz, M.Sc., and E. J. Ripling, Ph.D.

"The Stability of Mechanical Properties of Beta-Phase Magnesium-Lithium Alloys", by Professor W. R. D. Jones, D.Sc., and G. V. Hogg, B.Sc., Ph.D.

#### DISCUSSION ON "EFFECT OF COMPOSITION ON THE STRESS-CORROSION OF ALUMINIUM ALLOYS"

A discussion took place on the following two papers, which were presented by the authors.

"Stress-Corrosion of Wrought Ternary and Complex Alloys of the Aluminium-Zinc-Magnesium System", by R. Chadwick, M.A., F.I.M., N. B. Muir, B.Sc., A.I.M., and H. B. Grainger, B.Sc., A.I.M.

"Note on the Effect of Additions of Manganese and Chromium on the Microstructure of D.T.D. 687A-Type Alloys", by (Miss) M. K. B. Day, M.A., A.Inst.P., A.I.M.

At the conclusion of each session, votes of thanks to the authors and to the rapporteur were proposed by the Chairman and carried with acclamation.

#### VISITS

All-day visits were paid by delegates of the Italian and Swiss societies to the Research Laboratories and Glass Works of The General Electric Co., Ltd., Wembley, and to the A.P.V. Company, Ltd., and A.P.V. Paramount, Ltd., Crawley.

Delegates and ladies visited Windsor Castle, St. George's Chapel, and Eton.

#### BANQUET AND DANCE

In the evening, a Banquet and Dance was held in the Great Room, Grosvenor House, Park Lane, London, W.1, at which the Presidents, delegates, and members of the Italian and Swiss societies and their ladies were the guests of the Institute.

#### Friday, 3 May

##### VISITS

All-day visits were paid to Cambridge (the Colleges and other places of interest); the Research Laboratories of Associated Electrical Industries, Ltd., Aldermaston; the works of the Enfield Rolling Mills, Ltd., Brimsdown; the Ford Motor Co., Ltd., Dagenham; Northern Aluminium Co., Ltd., and Aluminium Laboratories, Ltd., Banbury; and Stewarts and Lloyds, Ltd., Corby.

#### Sunday, Monday, and Tuesday, 5, 6 and 7 May

##### PROVINCIAL VISITS

Delegates and ladies of the Italian and Swiss societies paid three-day visits to Birmingham or to South Wales.

*Birmingham.*—Visits were paid to: Stratford-on-Avon; the works and research laboratories of Imperial Chemical Industries, Ltd., Metals Division, Witton; the works of The General Electric Co., Ltd., Witton; the works of Henry Wiggin and Co., Ltd., and Research Laboratories of The Mond Nickel Co., Ltd., Birmingham; the works of Accles and Pollock, Ltd., Oldbury, and the Shaftsmoor Lane Works of Joseph Lucas, Ltd. Ladies also visited Warwick Castle and Broadway.

On the evening of Monday, 6 May, the visitors were entertained to dinner at the Welcome Hotel, Stratford-on-Avon, by the British Non-Ferrous Metals Federation.

*South Wales.*—Visits were paid to the Wye Valley and the Abbey and Margam Works and the Trostre Tinplate Works of The Steel Company of Wales, Ltd. Ladies also paid a day visit to the Gower Peninsula.

#### Wednesday, 8 May

A half-day visit was paid to the Calder Hall atomic energy station of the United Kingdom Atomic Energy Authority.

The meeting then concluded.

#### ANNUAL AUTUMN MEETING

16 to 20 September 1957

THE FORTY-NINTH ANNUAL AUTUMN MEETING of the Institute of Metals was held in Glasgow from Monday 16 to Friday 20 September 1957.

#### Monday, 16 September

##### VISITS

The meeting opened with a series of visits, in the afternoon, to the Mechanical Engineering Research Laboratories, East Kilbride, and to the works of Colvilles, Ltd., Ravenscraig; Fescol, Ltd., Port Glasgow; and Honeywell-Brown, Ltd., Newhouse.

##### OPENING SESSION

The Opening Session of the meeting was held at 6.0 p.m. at the Institution of Engineers and Shipbuilders in Scotland, 39 Elmbank Crescent, Glasgow, C.2, when the Chair was taken by Dr. H. HARRIS, B.Sc., A.R.C.S., D.I.C., Chairman of the Scottish Local Section.

Dr. HARRIS, on behalf of the Scottish Local Section; Sir Hector HETHERINGTON, K.B.E., D.L., M.A., LL.D., Principal of the University of Glasgow; and Sir Robert MACLEAN, President of the Glasgow Chamber of Commerce, welcomed members and their ladies. The President, Dr. L. B. PFEIL, O.B.E., A.R.S.M., F.I.M., F.R.S., replied to the speeches of welcome.

##### COCKTAIL PARTY

At the conclusion of the Opening Session, members and their ladies were the guests of the Scottish Local Section at a cocktail party.

#### Tuesday, 17 September

##### DISCUSSION ON "CREEP"

The meeting was resumed at the Institution of Engineers and Shipbuilders in Scotland at 10.0 a.m., when the President took the Chair.

A discussion was held on "Creep", based on the following five papers, previously published in the *Journal*. The papers were presented by Mr. C. R. TOTTLE, M.Met., F.I.M., who acted as Rapporteur:

"The Relation During Creep Between Grain-Boundary Sliding, Sub-Crystal Size, and Extension", by D. McLean, D.Sc., and M. H. Farmer, B.Sc.

"Calculation of the Contribution Made by Grain-Boundary Sliding to Total Tensile Elongation", by H. Brunner, Mech.Eng., and Professor N. J. Grant, Sc.D.

"A Note on the Metallography of Cracking During Creep", by D. McLean, D.Sc.

"The Effect of Heat-Treatment and Structure on the Creep and Stress-Rupture Properties of Nimonic 80A", by W. Betteridge, Ph.D., F.Inst.P., and A. W. Franklin, M.Sc., A.I.M.

"Intercrystalline Cracking in Creep of Some Aluminium Alloys", by B. J. Nield, B.Met., and Professor A. G. Quarrell, D.Sc., Ph.D., A.R.C.S., D.I.C., F.I.M.

At the conclusion of the session, the Chairman proposed, and there was carried with acclamation, a vote of thanks to the authors and to the rapporteur.

##### LUNCHEON

Members and their ladies were the guests of the Scottish Local Section at luncheon at the Central Hotel, Glasgow.

##### VISITS

In the afternoon, members paid visits to the works of Babcock and Wilcox, Ltd., Renfrew; G. and J. Weir, Ltd., Cathcart; and Henry Wiggin and Co., Ltd., Thornliebank, while ladies took part in coach tours via the Three Lochs, to Largs and the Ayrshire Coast, and to Loch Lomond and Drymen.

##### AUTUMN LECTURE

The President took the Chair at 8.30 p.m., at the Institution of Engineers and Shipbuilders in Scotland, when Dr. F. T. BARWELL, B.Sc.(Eng.), Wh.Sch., M.I.Mech.E., A.M.I.E.E., delivered the Twenty-Eighth Autumn Lecture on "Wear of Metals". At the conclusion, Dr. J. W. JENKIN proposed, and there was carried with acclamation, a vote of thanks to Dr. Barwell for his lecture.

Simultaneously, in another hall in the same building, Mr. Tom WEIR gave a talk, illustrated by lantern slides, to the ladies on "Scotland—an Explorer's Appreciation".

#### Wednesday, 18 September

##### VISITS, INCLUDING A VISIT TO EDINBURGH

In the morning, members and ladies proceeded by coach to Edinburgh, members visiting the works of The British Aluminium Co., Ltd., Falkirk, or those of Bruce Peebles and Co., Ltd., Edinburgh.



Lunch was taken at the North British Station Hotel, Edinburgh, when the Senior Magistrate welcomed the members and ladies to the City on behalf of the Lord Provost, Magistrates, and the Corporation of Edinburgh.

In the afternoon visits were paid to various places of interest in the City.

## CIVIC RECEPTION

In the evening, members and their ladies were the guests of the Lord Provost and Corporation of Glasgow at a Civic Reception in the City Chambers.

## Thursday, 19 September

### INFORMAL DISCUSSION ON "THE USE OF LIGHT ALLOYS IN SHIP CONSTRUCTION"

The meeting was resumed at 9.45 a.m. at the Institution of Engineers and Shipbuilders in Scotland, Glasgow, C.2, when there was an Informal Discussion on "The Use of Light Alloys in Ship Construction", arranged by the Metallurgical Engineering Committee. The Chair was taken by the Chairman of the Committee, Professor H. FORD, D.Sc., Ph.D., M.I.Mech.E. The discussion was opened by an introductory address by Mr. J. E. TOMLINSON, B.Sc., L.I.M.

## VOTES OF THANKS

At 12.0 noon, the President took the Chair, when Dr. Maurice COOK, F.I.M. (Past-President) proposed, and Mr. Christopher SMITH, F.I.M., seconded: "That the best thanks of the Institute of Metals be, and are hereby, extended to:

(i) The Chairman and Members of the Scottish Local Section for their kind invitation to the Institute to hold this Autumn Meeting in Glasgow.

(ii) Sir Andrew McCance, Dr. H. Harris, Mr. Matthew Hay, and the members of the Executive Committee for the excellent arrangements made for this meeting, and for the generous hospitality extended to members and their guests.

(iii) Lady McCance, Mrs. Harris, and the members of the Ladies' Committee for their thoughtful arrangements for the ladies.

(iv) The subscribers to the Reception Fund for their generosity.

(v) The Lord Provost, Magistrates, and Corporation of Glasgow for their welcome and generous hospitality.

(vi) The Lord Provost and Magistrates of Edinburgh for their welcome to Edinburgh.

(vii) Sir Hector Hetherington and Sir Robert Maclean for the welcome to Glasgow that they extended to members and their guests at the opening session.

(viii) The directors of the following establishments and companies for their invitations to members to visit their works and laboratories and for their hospitality:

Balcock and Wilcox, Ltd.

Barr and Stroud, Ltd.

The British Aluminium Co., Ltd.

Bruce Peebles and Co., Ltd.

Colvilles, Ltd.

Fescol, Ltd.

Honeywell-Brown, Ltd.

Mechanical Engineering Research Laboratories, Department of Scientific and Industrial Research.

North British Locomotive Co., Ltd.

University of Glasgow, Department of Natural Philosophy.

G. and J. Weir, Ltd.

Henry Wiggin and Co., Ltd.

(ix) The Committee of the Royal Scottish Automobile Club for placing the facilities of the Club at the disposal of members and their ladies for the duration of the meeting.

(x) The President and Council of the Institution of Engineers and Shipbuilders in Scotland for permitting the use of their building for the meeting and the Secretary and staff of the Institution for many courtesies.

(xi) All others who have contributed in any way to the success of this meeting."

The motion was put to the meeting and carried with acclamation.

Dr. H. HARRIS, Chairman of the Scottish Local Section, replied on behalf of the Institute's hosts.

## VISITS

In the afternoon, members visited the Department of Natural Philosophy of the University of Glasgow, and the works of Barr and Stroud, Ltd., Anniesland, and the North British Locomotive Co., Ltd., Springburn.

During the day the ladies took part in all-day coach tours, visiting Turnberry and Culzean Castle; The Trossachs; and Loch Lomond, Crianlarich, and Lochearnhead.

## DINNER-DANCE

In the evening, there was a Dinner-Dance at the Grosvenor Restaurant, Glasgow, at which the Honorary President of the Executive Committee, Sir Andrew McCANCE, F.R.S., presided.

The toast of "The Institute of Metals and the Non-Ferrous Metal Industries" was proposed by the Secretary of State for Scotland, The Right Hon. J. S. MACLAY, P.C., C.M.G., M.P.

At the conclusion of the dinner, the President presented to Dr. Maurice COOK, F.I.M., Past-President, the Institute of Metals (Platinum) Medal for 1957, in recognition of his outstanding contributions to the science of metallurgy, to the non-ferrous metal industry, and to the welfare of the metallurgical profession.

## Friday, 20 September

### SAIL ON THE CLYDE

Members and their guests took part in an all-day sail on the Clyde, in the *Queen Mary II*, during which presentations were made to the President and Mrs. PFEIL by the Reception Committee, and to Mr. Matthew HAY, Honorary Secretary of the Scottish Local Section, on behalf of the Council of the Institute.

The meeting then concluded.

## GENERAL MEETING

14 November 1957

A GENERAL MEETING of the Institute of Metals was held at the Headquarters of the Institute, 17 Belgrave Square, London, S.W.1, on Thursday, 14 November 1957, at 6.30 p.m. The Chair was taken by Dr. A. H. COTTRELL, F.R.S.

### LECTURE ON "THE LOW-TEMPERATURE DEFORMATION OF METALS"

The Chairman introduced Dr. T. H. BLEWITT, of the Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A., who delivered a lecture on "The Low-Temperature Deformation of Metals", which was followed by a discussion.

A vote of thanks to the lecturer was proposed by Professor R. KING and carried with acclamation.

The meeting then terminated.

# INAUGURAL MEETING OF THE POWDER METALLURGY JOINT GROUP OF THE IRON AND STEEL INSTITUTE AND THE INSTITUTE OF METALS

4 December 1957

THE INAUGURAL MEETING OF THE POWDER METALLURGY JOINT GROUP was held at Church House, Great Smith Street, London, S.W.1, at 10.30 a.m., on Wednesday, 4 December 1957. The Chair was taken at the opening session by Dr. Ivor JENKINS, F.I.M., Chairman of the Joint Group.

The Chairman made a statement on the aims of the Joint Group.

## LECTURE

The Chairman, Dr. Ivor JENKINS, F.I.M., then delivered a lecture on "Recent Developments in Powder Metallurgy".

## DISCUSSION ON "DEVELOPMENTS IN THE PRODUCTION AND QUALITY OF METAL POWDERS"

A discussion was held, based on the following brief papers. In the afternoon Mr. D. A. OLIVER, C.B.E., M.Sc., F.Inst.P., F.I.M., Deputy-Chairman of the Group, occupied the Chair.

"Atomization", by J. F. Watkinson, B.Met., Ph.D., A.I.M.

"Electrolytic Copper Powder", by E. Mehl.

"Electrolytic Production of Straight Metal Powders and Alloyed Metal Powders", by Ing. I. Ljungberg.

"The Manufacture of Metal Powders by the Gaseous Reduction of Metal-Bearing Solutions", by J. P. Warner.

"Mechanical Methods as Used in the Carbide Industry", by E. M. Trent, Ph.D., M.Met.

"Production of the Powders of Some of the Reactive Metals", by G. L. Miller, Ph.D., B.Sc., A.R.I.C.

At the conclusion of the meeting the Chairman proposed, and there was carried with acclamation, a vote of thanks to the authors of the papers.

## GENERAL MEETING

A GENERAL MEETING of the Institute of Metals was held at Harwell, Berkshire, on Monday and Tuesday, 9 and 10 December 1957.

## SYMPOSIUM ON "VACANCIES AND OTHER POINT DEFECTS IN METALS AND ALLOYS"

Monday, 9 December

### VISIT TO THE ATOMIC ENERGY RESEARCH ESTABLISHMENT, HARWELL

In the afternoon, members and delegates visited certain

aspects of researches in progress at the Atomic Energy Research Establishment and the reactors DIDO and PLUTO.

## LECTURE

The Chairman of the Metal Physics Committee, Professor H. O'NEILL, took the Chair when, at 5.0 p.m., Professor R. W. K. HONEYCOMBE, M.Sc., Ph.D., Professor of Physical Metallurgy, University of Sheffield, delivered an introductory lecture on "Vacancies and Other Point Defects" in the Cockcroft Hall, Harwell.

At the conclusion, Dr. A. H. COTTRELL, F.R.S., proposed, and there was carried with acclamation, a vote of thanks to Professor Honeycombe for his lecture.

Tuesday, 10 December

## SYMPOSIUM

The meeting was resumed at 9.45 a.m. in the Cockcroft Hall, Harwell, when Dr. H. M. FINNISTON, B.Sc., A.R.T.C., F.I.M. (Member of Council), occupied the Chair. Later in the morning, and at the afternoon session, the Chair was taken by Dr. A. H. COTTRELL, F.R.S.

The following papers, which had been published in advance of the meeting, were then presented and discussed:

"Point Defects and the Mechanical Properties of Metals and Alloys at Low Temperatures", by A. H. Cottrell, Ph.D., F.R.S.

"The Effects of Lattice Defects on Some Physical Properties of Metals", by T. Broom, M.A., Ph.D., and R. K. Ham, B.A.Sc.

"Point Defects and Diffusion in Metals and Alloys", by W. M. Lomer, M.Sc., Ph.D.

"Point Defects and Mechanical Properties of Ionic Crystals", by P. L. Pratt, B.Sc., Ph.D.

"Point Defects Near the Surface of a Metal", by E. C. Williams, M.Sc., A.Inst.P., and P. C. S. Hayfield, B.Sc., A.Inst.P.

"Point Defects and the Mechanical Properties of Metals and Alloys at High Temperatures", by D. McLean, D.Sc.

At the conclusion of the meeting, votes of thanks were proposed, and carried with acclamation, to the Director of the Atomic Energy Research Establishment for permitting the meeting to be held in the Cockcroft Hall and for the visit to the laboratories, and to the authors of the papers.

The meeting then terminated.

The papers (Serial Nos. 1781-1786) will be published, together with a report of the discussion, as *Monograph and Report Series* No. 23.



# THE PLASTIC DEFORMATION OF ALUMINIUM AND ALUMINIUM ALLOYS\*

1711

By G. THOMAS,† B.Sc., Ph.D., STUDENT MEMBER, and J. NUTTING,†  
M.A., B.Sc., Ph.D., MEMBER

## SYNOPSIS

The electron microscope has been used to study the metallography of slip in pure aluminium and aluminium alloyed with up to 7% magnesium, 5% silver, and 4% copper.

It has been found that the presence of magnesium and copper hinders the formation of lamellæ within the slip bands, whilst the presence of silver favours lamellæ formation, but lowers the lamellæ displacement. It has also been found that alloying elements influence the development of duplex slip.

The results are interpreted in terms of the mechanism for lamellæ formation outlined by Diehl, Mader, and Seeger (*Z. Metallkunde*, 1955, **46**, (9), 650). It is concluded that those elements which greatly distort the solvent lattice, prevent the formation of slip lamellæ and make more difficult the process of duplex slip. Consequently, the alloys work-harden more readily.

## I.—INTRODUCTION

THE first electron-metallographic study of slip in aluminium was reported by Heidenreich and Shockley<sup>1</sup> in 1947. Working with single crystals they found that the slip bands visible with the light microscope could be resolved into clusters of finer lines. These were interpreted as being terraces of small steps formed by slip on several parallel planes spaced some 100 atoms apart. The slip planes were looked upon as the boundaries of the slip lamellæ where each lamella had slipped over its neighbour a distance of about 1000 atoms. These experiments have been repeated, notably by Brown,<sup>2</sup> Nishimura and Takamura,<sup>3</sup> and Yakutovich *et al.*,<sup>4</sup> and their observations are generally in agreement with those of Heidenreich.

Brown<sup>2</sup> found that the separation of the lamellæ and their relative displacements within the slip bands did not alter appreciably with strain or rate of deformation, but that there was a slight increase in lamellæ displacement with increase in temperature. The most important observation was that the number of the lamellæ in the slip bands increased with increasing strain and with increasing temperature.

More recently the work of Kuhlmann-Wilsdorf and Wilsdorf<sup>5</sup> on the electron metallography of slip in aluminium, copper, and silver has shown that variations may occur in the amount of slip between each pair of lamellæ. Moreover, a new surface structure, which had not previously been detected by oxide-replica methods, was revealed by their technique of preparing silicon-monoxide replicas. This structure, designated the "elementary structure", consisted of very fine slip lines running across the surface between and parallel to slip bands. The spacing of these elementary lines was similar to the spacing of the lamellæ in the slip bands, but the height of the slip steps was less in the elementary structure than in the slip bands. The displacement of the lamellæ varied from a few to 1200 Å., but displace-

ments of 2000 Å., the value reported by Brown,<sup>2</sup> were never observed. Kuhlmann-Wilsdorf and Wilsdorf<sup>5</sup> pointed out that at normal strain rates and at room temperature aluminium is just in a boundary condition between deforming with and without an elementary structure. They also considered that slight changes in composition might influence the development of an elementary structure.

Previously Brown and Honeycombe<sup>6</sup> had shown that the slip characteristics of aluminium could be influenced by the surface treatment, and they suggested that the initial slip process involved small displacements on many lattice planes (fine slip) and that only with increasing deformation did slip bands begin to form. In the present investigation no fine slip on the scale reported by Kuhlmann-Wilsdorf and Wilsdorf<sup>5</sup> has been found in aluminium. Fine slip has, however, been observed in some of the alloys examined.

Apart from these authors' studies of  $\alpha$ -brass,<sup>5</sup> little has been reported on the electron metallography of slip in alloys. With this deficiency in view, the present research was undertaken to investigate the slip characteristics of alloys of aluminium containing magnesium, copper, and silver.

## II.—EXPERIMENTAL TECHNIQUES

### 1. MATERIALS EXAMINED

The materials investigated were pure aluminium, and alloys of aluminium containing magnesium, copper, and silver, respectively. Their compositions are given in Table I.

The aluminium, aluminium-magnesium, and aluminium-4% copper alloys were supplied in sheets rolled to a thickness of 1 mm. The aluminium-silver alloys, made up from the aluminium supplied and spectroscopically pure silver, were cast by diluting a master alloy of 50:50 composition.

\* Manuscript received 9 January 1956.

† Department of Metallurgy, Cambridge University.

## 2 Thomas and Nutting: The Plastic Deformation of Aluminium and Aluminium Alloys

The cast bars were cold rolled into strips 1 mm. thick. Small tensile test specimens having a gauge-length of

TABLE I.—Composition of Alloys Used.

Material	Cu, %	Mg, %	Si, %	Fe, %	Mn, %	Ti, %	Ag, %
Al . . .	...	...	<0.001	0.0015	0.0005	...	...
Al-1% Mg .	0.004	1.01	0.02	0.007	0.002	0.002	...
Al-3% Mg .	0.004	3.06	0.02	0.012	0.002	0.002	...
Al-5% Mg .	0.003	5.12	0.014	0.007	0.001	0.002	...
Al-7% Mg .	0.005	6.50	0.015	0.005	0.002	0.002	...
Al-1% Ag .	...	...	0.001	0.0015	...	...	1.01
Al-5% Ag .	...	...	0.001	0.0015	...	...	4.61
Al-4% Cu .	3.7	...	0.001	0.0015	0.0005	...	...

1 in. were stamped from these sheets and after the heat-treatments were elongated in a Hounsfield tensometer. All the specimens were polycrystalline.

All the alloys were polished electrolytically in a solution of 4 parts ethyl alcohol to 1 part 60% perchloric acid. Polishing was usually carried out under a potential of 25-30 V. With the aluminium-4% copper specimens the brown surface films that formed during polishing were removed by swabbing in ammonia or nitric acid.

The specimens were etched in Lacombe and Beaujard's reagent (aqua regia + 3% HF). This etch produces pits on the surface of the materials with sides parallel to {100}, and these enabled the surface orientation to be determined. It was not possible to obtain replicas from the aluminium-silver alloys after this etching treatment because a black tenacious film formed which could not be removed. These alloys were examined, therefore, in the unetched condition.

After etching, the specimens were elongated by in-

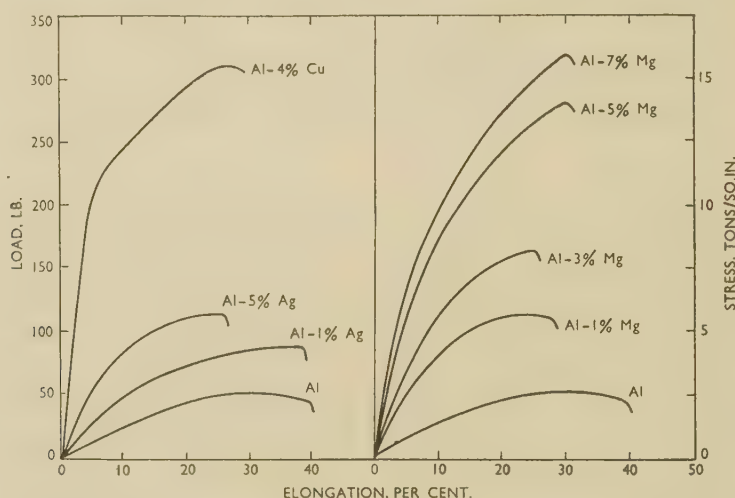


FIG. 1.—Load/Elongation Curves for Aluminium and Aluminium Alloys.

### 2. HEAT-TREATMENTS

The solution heat-treatments for the aluminium-magnesium alloys consisted of a 4-hr. soak at 425° C. followed by water-quenching. The aluminium-copper alloys were given a similar treatment at 535° C., and the aluminium-silver alloys were quenched after 4 hr. at 420° C.

The pure aluminium specimens were normally annealed for 3 hr. at 600° C. Some coarse-grained specimens were prepared by deforming 3% after this heat-treatment, followed by annealing for 21 hr. at 620° C. This treatment gave about 3 grains over the gauge-length of the test specimen, which would then elongate for 80% before fracturing. Some aluminium and aluminium-7% magnesium specimens were deformed at a low temperature by arranging the Hounsfield tensometer vertically and surrounding the test specimen with liquid air contained in a Tufnol tube.

### 3. REPLICA TECHNIQUES

The oxide-replica technique was used in this investigation. The sequence in the preparation of the replica was: electropolishing after heat-treatment, etching (when possible), deforming, anodizing, and stripping of the oxide film.

crements of 5% up to the point of fracture. The load/elongation curves for all the materials examined are shown in Fig. 1. These were obtained by continuous deformation to fracture.

Anodizing after deformation was carried out in a solution of 12% disodium hydrogen phosphate containing 0.5% sulphuric acid, at a potential of 27-30 V. This gave an oxide film 250-300 Å. thick. The films were stripped by immersion in saturated mercuric chloride, washed in 10% hydrochloric acid, then in distilled water, captured on copper grids, and finally dried. Unfortunately this method destroys the specimen, so that successive stages in the deformation of the same specimen could not be followed using this technique.

Resolutions of 50 Å. were regularly obtained when these oxide films were used as replicas in the Siemens U.M. 60C electron microscope.

## III.—EXPERIMENTAL RESULTS

### 1. ALUMINIUM

As found by other workers, the coarse slip bands were resolved into clusters of lamellæ, but no fine slip or elementary structure of the type described by Kuhlmann-



Wilsdorf and Wilsdorf<sup>5</sup> has been detected in aluminium deformed at room temperature.

Where the orientation of the surface was known from examination of the etch pits, the slip displacements ( $x$ ) of {111} planes in the slip direction were obtained by dividing the measured slip-line width ( $s$ ) by the cosine

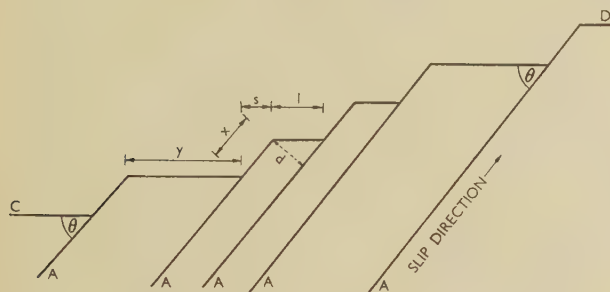


FIG. 2.—Diagram Illustrating the Formation of Slip Lamellae and the Measurement of Slip Quantities.

CD = free surface. AA = active slip planes.

of the angle ( $\theta$ ) subtended by the slip plane at the surface. The true lamellar separation ( $d$ ) was calculated by multiplying the measured width ( $l$ ) by the sine of the angle. The interband separation ( $y$ ) was measured directly as the perpendicular distance between adjacent bands. A diagram illustrating the measurements made is given in Fig. 2.

Measurements of these properties have been carried out on specimens elongated by increments of 5% up to 80% at room temperature and up to 12% at the temperature of liquid air, when fracture occurred.

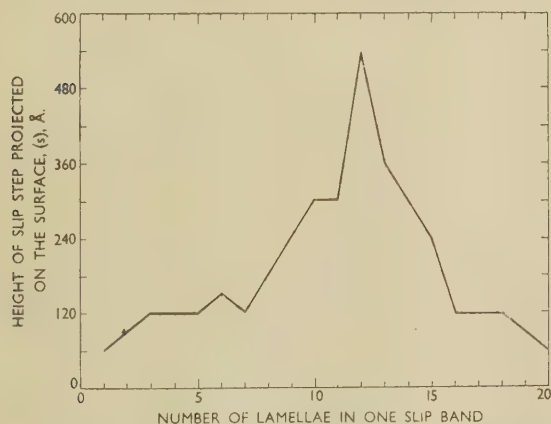


FIG. 3.—The Variation in Slip Displacement of Individual Lamellae in a Slip Band in Aluminium Elongated 80% at Room Temperature. Average value of  $s = 200$  Å.; average slip distance = 340 Å.

The actual measurements were made on the electron micrographs. For each specimen three or four photographs were taken of regions within one grain, and mean values were obtained for the band separation ( $y$ ), for the primary slip displacement ( $x$ ), and for the lamellar separation ( $d$ ). With large strains the primary slip displacement of the lamellae within the slip bands varied and was usually greater at the centre of the band than at the edges. This effect is illustrated in Fig. 3, the measurements for which were obtained from the electron micrograph reproduced in Fig. 4 (Plate I).

From a knowledge of the band separation, the number of lamellae per band, and the primary slip distance, it is possible to calculate the elongation of the grain resulting from the primary slip. This value may not correspond to the macroscopic elongation; it may be smaller because of duplex slip or of the presence of fine unresolved slip, or it may be larger because of heterogeneity of the strain in different grains. The results of the various measurements and calculations are given in Table II.

TABLE II.—Calculation of Slip Quantities in Pure Aluminium.

Linear Elongation, %	Lamellar Separation ( $d$ ), Å.	Average Primary Slip Displacement ( $x$ ), Å.	Number of Lamellae per Band ( $n$ )	Average Band Separation ( $y$ ), $\mu$	Calculated Elongation $\frac{n \times s}{y + (n \times l)} \times 100$ , %	Illustration
5	250	600	$\approx 4$	1.9	7	...
10	250	600	$\approx 9$	1.9	15	...
15	250	620	$\approx 9$	1.7	15	...
20	300	720	9-14	1.9	18	...
25	270	630	$\approx 14$	1.7	24	...
40	300	650	$\approx 14$	1.5	28	...
80	300	340	20-30	0.8	60	Fig. 4 *
Deformed in liquid air						...
12	570	1400	1-2	$\frac{1}{2}$ -1 $\frac{1}{2}$	8	Fig. 21 †

\* Plate I.

† Plate III.

#### (a) Fine Structure

There was some evidence of a fine structure in aluminium deformed at the temperature of liquid air, and in a few of the specimens deformed at room temperature. However, the evidence is insufficient to support the conclusions of Kuhlmann-Wilsdorf and Wilsdorf,<sup>5</sup> but is in agreement with the conclusions of Brown and Honeycombe<sup>6</sup> that there is no further development of fine slip with increasing deformation.

#### (b) Primary Slip

The term primary slip is used to indicate slip occurring on the first-activated slip planes, and therefore excludes slip on planes other than those parallel to the first-activated planes. From the results given in Table II, it can be seen that the mean primary slip distance does not alter appreciably with strain. These mean values are, however, lower than those quoted by Brown,<sup>2</sup> but more lamellae have been resolved in the slip bands, hence the overall slip displacement per band (i.e.  $n \times x$ ) corresponds to Brown's results.

### 2. SOLID SOLUTIONS OF ALUMINIUM-MAGNESIUM ALLOYS

The slip quantities for aluminium-magnesium alloys are given in Table III. From these results it can be seen that the effect of magnesium in solid solution is most marked in altering the slip characteristics of aluminium. In general, there is a tendency to reduce the number of lamellae in each band until with 7% magnesium slip occurs in single slip lines. These slip lines are not separated by constant distances, and there is great variation from the mean values quoted in Table III. The mean slip displacement increases with

magnesium additions, but in all cases appears to be independent of strain. When, after severe deformation slip lamellæ are produced, the lamellar separation decreases with increasing magnesium content but does not

TABLE III.—Calculation of Slip Quantities in Aluminium-Magnesium Alloys.

Alloy	Linear Elongation, %	Lamellar Separation (d), Å.	Average Primary Slip Displacement (x), Å.	Number of Lamellæ per Band (n)	Average Band Separation (y), μ	Calculated Elongation $\frac{n \times s}{y + (n \times l)} \times 100, \%$	Illustration
Al-1% Mg	10	270	580	1-2	1.3	5	Fig. 5 *
	15			2-3	1.3	7	...
	20			2-4	1.3	10	Fig. 6 *
	25			3-5	0.6	19	...
	30			4-5	0.6	23	...
	35			4-6	0.15	65	...
Al-3% Mg	10	160	1000	1-2	1.7	3.5	...
	15			1-2	1.7	7	Fig. 7 *
	20			1-3	0.6	27	...
	25			2-4	0.3	50	Fig. 8 *
	30			2-4	0.3	50	...
	35			2-4	0.3	50	...
Al-5% Mg	10	160	1150	1-2	1.7	12	...
	15			1-2	0.8	25	Fig. 9 *
	20			1-2	0.4	50	...
	25			1-2	0.3	50	Fig. 10 *
	30			1-3	0.3	58	...
	35			1-3	0.3	58	...
Al-7% Mg	5	...	1350	1	2.3	3.5	...
	10			1	2.0	4	...
	15			1	1.3	6	...
	20			1	0.7	11	Fig. 11 *
	25			1	0.7	11	...
	30			1	0.3	26	...
	35			1-2	0.3	26	Fig. 12 †
	40			1-3	0.1	78	Fig. 13 †
	40			1-3	0.1	78	...

\* Plate I.

† Plate II.

vary with deformation. Electron micrographs illustrating the various slip characteristics are reproduced in Figs. 5-13 (Plates I and II).

With increasing deformation the slip lines tend to become wavy, whilst at constant deformation the waviness becomes more marked with increasing magnesium content. In one or two instances a fine structure between the slip bands has been observed. As in aluminium, when lamellæ formation occurred, the slip displacements of the central lamellæ were greater than those at the edges.

Some specimens of aluminium-7% magnesium were deformed at liquid-air temperature, when elongations of about 30% were obtained before fracture, a value about three times greater than that found with pure aluminium. Slip occurred in single coarse slip lines on which the slip displacement was about 1100 Å. A typical microstructure is shown in Fig. 14 (Plate II).

### 3. SOLID SOLUTIONS OF ALUMINIUM-SILVER ALLOYS

Aluminium alloys containing 1% and 5% silver were examined in a way similar to that described previously. The orientations of the free surfaces were not obtained in these alloys, as satisfactory etch pits could not be produced. In all the aluminium-silver alloys fine slip was clearly observed, but the results given in Table IV refer only to the slip which resulted in band formation. Typical electron micrographs are shown in Figs. 15-17 (Plate II). It can be seen by comparing the results for the aluminium-silver alloys with those for aluminium-magnesium alloys, that silver has almost the opposite effect to that of magnesium. With silver in solid solu-

tion the slip displacement is smaller than with any of the other systems examined, and is of the same order as that found in the elementary structures reported by Kuhlmann-Wilsdorf and Wilsdorf.<sup>5</sup> The tendency for lamellæ formation is very marked in aluminium-silver alloys, thus as many as 30 lamellæ have been observed in one band after 25% elongation.

TABLE IV.—Calculation of Slip Quantities in Aluminium-Silver Alloys.

Alloy	Linear Elongation, %	Lamellar Separation (l), Å.	Average Height of Slip Steps in Bands (s), Å.	Number of Lamellæ per Band (n)	Average Band Separation (y), μ	Calculated Elongation $\frac{n \times s}{y + (n \times l)} \times 100, \%$	Illustration
Al-1% Ag	5	130	70	≤6	2.2	2	...
	10			≤6	2.0	2.2	Fig. 15 *
	15			6-8	0.4	11	...
	20			≤10	0.4	13	...
	25			10-20	0.4	16	...
Al-5% Ag	5	130	70	≤12	1.5	1.3	Fig. 16 *
	10			≤15	0.6	13	...
	15			≤15	0.4	18	...
	20			10-30	0.25	23	...
	25			10-30	0.25	28	Fig. 17 *

\* Plate II.

The electron micrographs reproduced in Figs. 15-17 show surface markings other than those resulting from slip. Small white spots are present in the background, similar to those observed in aluminium-copper alloys. Koda and Takeyama<sup>7</sup> have also observed white spots in oxide replicas from aluminium-silver alloys, and they believe them to correspond to the spherical aggregates of silver atoms detected by Walker and Guinier<sup>8</sup> in these alloys using X-ray-diffraction techniques.

### 4. SUPERSATURATED SOLID SOLUTIONS OF ALUMINIUM-4% COPPER

When this alloy is plastically deformed only coarse single slip lines are found. The slip displacements may vary over a wide range. Thus, values between 800 and 2500 Å. have been found, and there was no constant relationship between slip displacement and the strain. Similarly, the slip lines were not uniformly spaced and were wavy, and slip did not appear to occur on well-defined crystallographic planes. Some typical micrographs of the slip lines are shown in Figs. 18 and 19 (Plate II).

As with the aluminium-silver alloys, white spots, having a dia. of 200-300 Å., were observed on the replicas from these alloys even when examined as soon as possible after the quenching treatment. The present authors<sup>9</sup> have suggested that these spots result from the segregation of copper atoms at the solution-treatment temperature. However, the slip characteristics of these alloys are completely different from those of aluminium-silver alloys where solute clustering is also believed to occur. It is of interest to note that only a few white spots are observed on the new surfaces created by the slip displacement and adjacent to the slip lines.

### 5. DUPLEX SLIP

Duplex slip was observed in all the alloys when the elongation exceeded 5-10%. Generally, the number of



lamellæ in the second slip system was less than that in the first, but the total displacement on the second system relative to the first usually increased with increasing deformation. Thus, in pure aluminium dis-

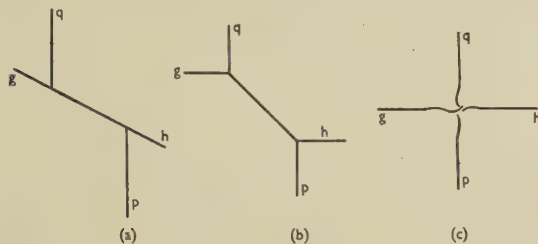


FIG. 24.—Schematic Representation of the Form of Duplex Slip-Line Intersections. (a) Simple faulting; (b) double faulting; (c) complex faulting.

$pq$  = primary slip lines.

$gh$  = secondary slip lines.

placements on the second system of 11,000 Å. have been noted after 40% elongation (Fig. 20, Plate III).

Two simple geometrical possibilities may be considered for the development of duplex slip. After deformation on one system, the second system begins to operate and no further deformation occurs on the primary system. The resulting microstructure will then show only a direct translation of the primary slip lines. This can be described as simple faulting, and is illustrated schematically in Fig. 24 (a). Alternatively, small movements on both the first and second systems may occur simultaneously or consecutively, and the resulting microstructure will show the translation of both slip lines. This can be described as double faulting, and is illustrated schematically in Fig. 24 (b).

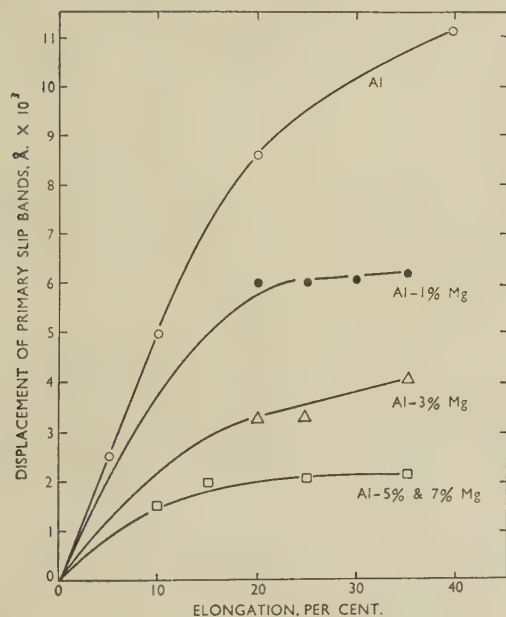


FIG. 25.—The Effect of Increasing Deformation upon the Displacement of the Primary Slip Bands During Duplex Slip in Aluminium and Aluminium-Magnesium Alloys.

Simple faulting has been observed chiefly in the aluminium-silver alloys, and a typical electron micrograph is shown in Fig. 17 (Plate II). Double fault-

ing has been found in the aluminium and aluminium-magnesium alloys, and an example is given in Fig. 8 (Plate I). However, other more complicated forms of simple and double faulting have been found. One of the most common of these is illustrated diagrammatically in Fig. 24 (c), and an example is shown in Fig. 21 (Plate III).

The effect of increasing deformation upon the displacement of the primary slip lines by slip on the second system is influenced by the magnesium content of the aluminium, as is shown in Fig. 25. Thus, increase in magnesium lowers the amount of displacement on the

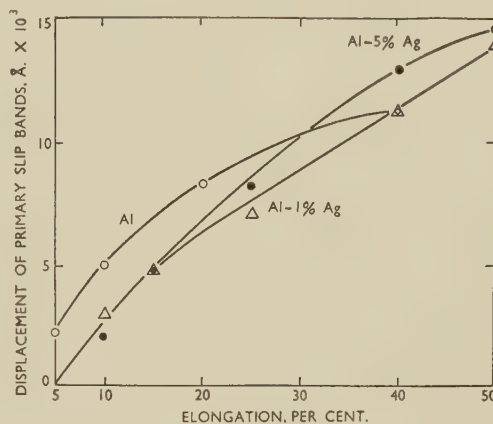


FIG. 26.—The Effect of Increasing Deformation upon the Displacement of the Primary Slip Bands During Duplex Slip in Aluminium and Aluminium-Silver Alloys.

second system for a given macroscopic strain, whilst with 5 and 7% magnesium the displacement increases with strain to a given value, after which no further deformation along the second slip plane occurs. Thus, new slip planes must become operative as the elongation is increased.

The aluminium-silver alloys behaved in a similar way to the pure aluminium, in that the amount of slip on the second system increased with increasing deformation, as shown in Fig. 26. Duplex slip was not often found in aluminium-4% copper alloys. Where duplex slip occurred, both the primary and secondary lines were wavy and exhibited only single slip steps. Usually the secondary slip lines did not progress across a whole grain, but stopped after one or two intersections with the primary bands. An example is given in Fig. 22 (Plate III).

#### IV.—DISCUSSION

##### 1. PRIMARY SLIP AND LAMELLÆ FORMATION

Various theories have been put forward to account for the formation of slip lamellæ in pure aluminium during plastic deformation. Brown<sup>10</sup> believed that slip caused hardening of the metal immediately adjacent to the slip plane, but that at a distance of 100 atoms or so, softening occurred; thus with increasing deformation further slip took place in this softened region. Mott<sup>11</sup> extended this idea by assuming that the softening was caused by the diffusion of vacancies formed on the original slip plane by the passage of dislocations. The latter view would appear unlikely, since lamellæ formation can occur

at low temperatures when the diffusion of vacancies would not readily take place.

Cottrell<sup>12</sup> and Fisher, Hart, and Pry<sup>13</sup> have suggested that because of duplex slip, the outer part of the original slip plane may be displaced relative to the dislocation source. If this source then continues to produce dislocations they will reach the surface on a new plane displaced from the original plane by the distance of movement on the second system. Whilst there is some evidence for this type of mechanism (see Fig. 23), it cannot be generally applicable, as all metals would be expected to show lamellated slip bands, and the present work proves that this is not the case.

The view of Kuhlmann-Wilsdorf, van der Merwe, and Wilsdorf<sup>14</sup> is that the slip bands are a further development of the fine structure. They consider that after the formation of the fine structure by the flow of dislocations from many sources, particular sources become active. The dislocations from these active sources neutralize those from other inactive sources on the same slip plane; thus a dislocation-free band is produced which allows the sources on neighbouring planes to become active again, and slip lamellæ are produced, having the same separation as that of the original fine structure. To account for the slip behaviour of  $\alpha$ -brass, which shows coarse slip lines and neither fine structure nor slip lamellæ, Kuhlmann-Wilsdorf and Wilsdorf<sup>5</sup> have to postulate that there are only a few dislocation sources which may become active under the action of a stress. These sources can continue to act and produce many dislocations before they become inactive as a result of changes in the resolved shear stress. Although Kuhlmann-Wilsdorf and Wilsdorf can provide some experimental evidence to support their views explaining the absence of dislocations between the slip lines in deformed  $\alpha$ -brass, similar evidence is not obtained with an aluminium-7% magnesium alloy, but this also deforms to a considerable extent without the production of lamellated slip bands.

An entirely different approach has been adopted by Diehl, Mader, and Seeger.<sup>15</sup> They have assumed that dislocations are produced from a source until the interaction stress from the dislocations is sufficient to force one of the dislocations on the original slip plane to form a loop along another slip plane, but one on which the resolved shear stress is not so great. As this loop grows away from the original slip plane, it will assume the characteristics of another dislocation source on a slip plane parallel to the original plane. Consequently, new dislocations will be produced on this plane. This process can then be repeated, so producing lamellated slip bands. A mechanism of this type can be adapted to account for the present results.

As was pointed out by Brown,<sup>10</sup> when aluminium is deformed, the strain may be obtained by the development of new bands or by the formation of lamellæ adjacent to the first-formed bands. This implies that there is no shortage of dislocation sources from which bands can form, but that under differing loading conditions the relative amount of strain arising from either lamellæ formation or the activation of new sources may be changed. The mechanism suggested by Diehl, Mader, and Seeger<sup>15</sup> would imply that increasing strain is accommodated only by increasing lamellæ formation, but this is obviously not the case, because in deforming

at room temperature the number of slip bands definitely increases with strain. Therefore, it must be concluded that the stress required to form lamellæ increases as the number of lamellæ in the band increases.

If the mechanism of lamellæ formation outlined by Diehl, Mader, and Seeger<sup>15</sup> is accepted, then it would appear that alloying elements in solid solution may influence the stress required to make a dislocation move away from the original slip plane. The other possibility would be that the alloying elements influence the stress required to activate new sources, i.e. the solute elements may form a dislocation atmosphere. But in all the alloys examined the solute concentration was much greater than would be required for forming the atmospheres, and therefore the slip patterns would not be greatly influenced by solute concentration. A further difficulty is that dislocation locking would apply to the sources rather than to the newly formed dislocations. This would make it more difficult to activate the sources, thus lamellæ formation should take place in preference to the development of new bands, and this is obviously not the case. It must be concluded therefore that the effect of the alloying elements is to prevent the dislocations leaving their original slip planes.

The factor which appears to influence the ease with which the dislocations may leave their slip planes is the distortion of the lattice produced by the solute element. Axon and Hume-Rothery<sup>16</sup> have shown that the addition of magnesium to aluminium increases the lattice parameter, silver has little effect, whilst copper decreases the lattice parameter. The effect of lattice strain can therefore now be correlated with the slip behaviour. With increasing magnesium content, the resulting increase in distortion makes it more difficult for lamellæ to form, so that new bands are produced to accommodate the strain. A somewhat similar effect is found when copper is added to aluminium, although the behaviour of this alloy may be complicated further by the solute clustering which is thought to occur. With silver additions, where very small changes only in lattice parameter take place, the alloy behaves in the same way as pure aluminium, i.e. lamellæ formation is favoured. Although solute clustering is thought to occur in aluminium-silver alloys, as the lattice strain will be small the clusters will not act as obstacles to the flow of dislocations.

## 2. DUPLEX SLIP AND WORK-HARDENING

Although it has not been possible to measure the total amount of deformation taking place on systems other than the one first activated, it does appear that the mode of deformation on the second system is different from that on the first system. Lamellæ formation is more difficult on the second system, whilst it seems that rather than bands being formed, i.e. new sources being activated, the strain is accommodated by continued deformation along the first-formed bands of the second system. At large strains, however, a limit is reached to the amount of deformation that can occur along the first-formed bands and new bands must be produced. With increasing additions of magnesium to the aluminium, the amount of displacement in the bands of the second system is progressively reduced, whilst with silver additions, the behaviour is similar to that of pure



aluminium. Thus again lattice distortion rather than simply the presence of foreign atoms appears to influence the development of duplex slip.

The fact that band formation rather than lamellæ formation occurred when deforming aluminium at low temperatures, whilst the reverse was the case at high

least work-hardening is found in the aluminium and aluminium-silver alloys which exhibit the greatest tendency to lamellæ formation. The question now arises: what is the significance of these observations?

The more recent theories suggest that the interaction of dislocations produced on intersecting slip planes is responsible for work-hardening. In view of the fact that the slip displacements on the secondary slip system are reduced by the addition of magnesium to aluminium it may be concluded that the presence of magnesium makes it more difficult for duplex slip to occur. The dislocations on the primary and secondary systems interact more strongly, and therefore the alloys work-harden more readily than pure aluminium.

The mechanism of lamellæ formation outlined by Diehl, Mader, and Seeger<sup>15</sup> involves dislocation movements very similar to those involved in duplex slip. It has already been suggested that alloying elements which strain the aluminium lattice prevent lamellæ formation, and therefore it would be expected that they would also render duplex slip a more difficult process. The significance of the fact that band formation, rather than lamellæ formation, occurs in alloys which work-harden strongly, now becomes clear. If the strain on the primary system is accommodated by band formation rather than lamellæ formation it is an indication that duplex slip will be a difficult process, and the alloy will therefore work-harden readily.

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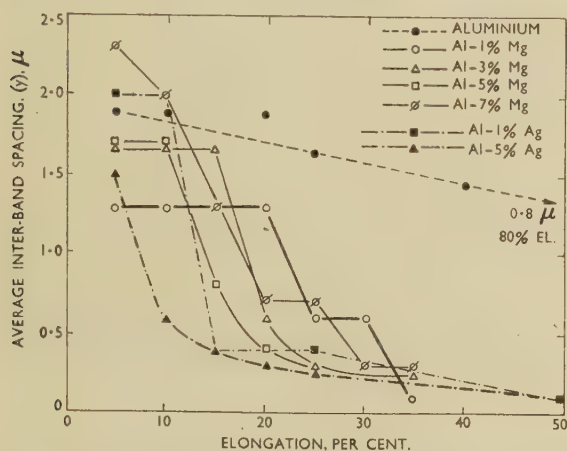


FIG. 27.—The Effect of Increasing Deformation upon the Inter-Slip-Band Spacing in Aluminium, Aluminium-Magnesium, and Aluminium-Silver Alloys.

temperatures, led Brown<sup>10</sup> to the conclusion that work-hardening was associated more with band formation than with lamellæ formation. From the present investigation the same conclusion may likewise be drawn. This can be inferred from Fig. 27 which shows the change in band spacing with strain. As can be seen from Fig. 1 the greatest work-hardening is found in the aluminium-magnesium and aluminium-copper alloys, which also show the least tendency to lamellæ formation, whilst the

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# 1712 THE REFINEMENT OF CAST GRAIN-SIZE IN COPPER-ALUMINIUM ALLOYS CONTAINING 7-9 PER CENT. ALUMINIUM \*

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## SYNOPSIS

Attempts to obtain grain refinement in copper-aluminium alloys containing 7-9% aluminium, by the introduction of selected nucleating compounds, have shown that in the alloys in which the  $\alpha$  phase solidifies first, moderate refinement may be produced by additions of molybdenum, niobium, tungsten, or vanadium of the order of 0.1%.

The addition of 0.02% of boron gave very considerable grain refinement in alloys in which the  $\beta$  phase was the first to solidify. Owing to an undercooling effect, this type of refinement can also be obtained in certain hypo-eutectic alloys. The grain-refined material has improved hot-working properties.

## I.—INTRODUCTION

THE literature on the mechanism of grain refinement in castings has been reviewed in a previous paper by the present authors <sup>1</sup> and in a more recent paper by Cibula.<sup>2</sup>

The work now described represents an attempt to apply the nucleation theory, due mainly to Cibula,<sup>3,4</sup> to a limited range of copper-aluminium alloys.

In both laboratory and industrial experiments, coarse-grained columnar billets normally produced in binary copper-aluminium alloys in this range showed a marked tendency to surface cracking at columnar boundaries during the early stages of either hot rolling or forging. Corresponding billets having an equi-axial structure were completely free from such cracks.

## II.—SELECTION OF POSSIBLE INOCULANTS

TABLE I.—Possible Inoculants for  $\alpha$ -Phase Copper-Aluminium Alloys.

Compound	Structure	Lattice Dimensions, Å.	Lattice Misfit, %*
$\alpha$ Cu-Al (7.5% Al)	F.c.c.	$a_0 = 3.657$	—
AlB <sub>2</sub>	Hex. c.p.	$a_0 = 3.00, c_0 = 3.25^*$	-11
CaB <sub>6</sub>	Cubic	$a_0 = 4.15$	+13
CeB <sub>6</sub>	"	$a_0 = 4.13$	+13
CeC <sub>2</sub>	Tetragonal	$a_0 = 3.87$	+6
CoB	Orthorhombic	$a_0 = 3.95$	+8
Co <sub>2</sub> B	?	$a_0 = 5.00, c_0 = 4.21^*$	+15
Mo	Cubic	$a_0 = 3.14$	-14
MoC	Interstitial hex. c.p.	$c_0 = 2.99$	-18
Nb	Cubic	$a_0 = 3.294$	-10
NbC	Interstitial f.c.c.	$c_0 = 3.14$	-14
TiB <sub>2</sub>	Hex. c.p.	$a_0 = 3.03, c_0 = 3.23^*$	-12
TiC	Interstitial f.c.c.	$c_0 = 2.99$	-18
V	Cubic	$a_0 = 3.04$	-17
VO	Interstitial f.c.c.	$c_0 = 3.04$	-17
W	Cubic	$a_0 = 3.16$	-14
WC	Hex. c.p.	$c_0 = 2.89$	-20
W <sub>2</sub> C	Interstitial	$a_0 = 2.99$	-18
ZrB <sub>2</sub>	Hexagonal	$a_0 = 3.17$	-13
ZrC	Interstitial f.c.c.	$c_0 = 3.32$	-10

\* Where more than one lattice parameter is given, misfit is calculated only for the parameter marked with an asterisk.

Table I gives the range of inoculants chosen for addition to the all- $\alpha$  7.5% aluminium series. Inoculants having lattice misfit of up to 20% were used, this being of the same order as for the previous work <sup>1</sup> on alloys in which the  $\beta$  phase solidified first. Most of the compounds selected were carbides or borides formed by the transition metals and were similar to metals in structure. All had melting points above that of copper.

For alloys in the region of the eutectic composition (8.5% aluminium) additions of 0.02% boron were made with the object of nucleating crystals of the  $\beta$  phase by the formation of B<sub>4</sub>C in the melt. This had previously been shown to give considerable refinement in all- $\beta$  alloys.<sup>1</sup>

## III.—EXPERIMENTAL WORK

Two series of melts were prepared. A nominal content of 7.5% aluminium was fixed for the first series, in which the effect of  $\alpha$ -phase inoculants was studied. The actual aluminium contents in this series varied in the range 7.3-7.65%, but all the alloys were entirely single-phase (Table II).

The second series consisted of six ingots (Table III) having a range of aluminium contents from 8.04 to 8.71%, and included one hypo-eutectic and one hyper-eutectic standard.

All the casts were prepared from a copper-aluminium master alloy containing Al 12.27, Fe 0.07, Si 0.04, Zn 0.02%, balance copper, and a high-purity copper containing Ni 0.01, O 0.019, Bi 0.0003%, As trace, Cu 99.96%.

A 7.5% aluminium alloy prepared from these materials was compared with one in which the aluminium was added as super-purity metal (99.99%). Identical structures were obtained, showing that the small amount of iron introduced in the former alloy had no grain-refining effect. A similar result had previously been obtained for a 10% aluminium alloy.<sup>1</sup>

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# Refinement of Cast Grain-Size in Cu-Al Alloys Containing 7-9 Per Cent. Aluminium 9

The various additions were wrapped in copper foil and added to the melt in the furnace. Analyses of the materials used are given below :

**Boron** (as copper-base alloy) :

B 4.75, Cu 93.7, Si 0.6, Fe 0.06, Mg 0.20%, traces Mn and Pb.

**Calcium** (pure metal).

**Cerium** (as Mischmetall) :

Ce 51-53, Nd 15-17, Pr 3-4, La 22-25, Sm 2-3, Y + Tb 3, Fe 5, C 0.05, CaC<sub>2</sub> 0.02, Ca 0.02%, traces Al and Si.

**Cobalt** (as copper-base alloy) :

Co 12.0, Ni 0.20%, balance Cu.

**Molybdenum** (as aluminium-base alloy) :

Mo 10.0, Fe 0.5, Si 0.5%, balance Al.

**Niobium** (as aluminium-base alloy) :

Nb 59.25, Ta 6.60, Fe 2.19, Si 0.95, Ti 0.60%, balance Al.

**Titanium** (as aluminium-base alloy) :

Ti 10.3, Fe 0.47, Si 0.33, Cu 0.08%, balance Al.

**Tungsten** (as aluminium-base alloy) :

W 5.4, Fe 0.4, Si 0.3%, balance Al.

**Zirconium** (as aluminium-base alloy) :

Zr 8.2, Ti 0.2, Fe 0.5, Si 0.35, Cu 0.1%, balance Al.

**Vanadium** (as aluminium-base alloy) :

V 10.6, Fe 0.4, Si 0.5%, balance Al.

In the present series of tests, a pouring temperature of 1120° C. was adopted for the  $\alpha$ -alloys and 1100° C. for the ( $\alpha + \beta$ ) alloys. These temperatures were sufficiently high to ensure completely columnar structures in all cases where grain refinement had not occurred.

All the laboratory ingots were cylindrical, 3 in. in dia.  $\times$  8 in. long, and were cast by the Durville process. Full details of fabrication are given in the earlier paper.<sup>1</sup> The results then obtained on alloys in which the  $\beta$  phase solidified first and was nucleated by B<sub>4</sub>C, had indicated that sufficient carbon was present in the melt to react with additions to form carbides. However, in the current tests, a surface covering of wood charcoal was maintained during melting.

The ingots were sectioned and examined as before.

## IV.—RESULTS ON GRAIN REFINEMENT

### 1. ALL- $\alpha$ ALLOYS

The results given in Table II show that grain refinement was produced only in ingots to which molybdenum, niobium, tungsten, or vanadium had been added. Although the percentages of the various additions were increased from the 0.01% (found effective in the case of boron in duplex copper-aluminium alloys) to 0.1% in selected instances, no improvement was obtained.

Figs. 1 (a) and (b) (Plate IV) compare the standard structure with that obtained by an addition of 0.1% vanadium.

### 2. ( $\alpha + \beta$ ) ALLOYS IN THE REGION OF THE EUTECTIC

#### (a) Laboratory Tests

The results given in Table III indicate that grain refinement may be obtained in hypo-eutectic alloys in which the  $\alpha$  phase would normally solidify first, by the formation of B<sub>4</sub>C, which nucleates and causes the preferential solidification of the  $\beta$  phase. It appears that, under these experimental conditions, a certain amount of undercooling of the molten alloy occurs, until a tempera-

ture is reached at which  $\beta$  solidification can be nucleated (by extension of the  $\beta$ -phase liquidus below and beyond the eutectic point). When the aluminium content is reduced to a point between 8.04 and 8.25%, insufficient undercooling is possible, and the  $\alpha$  phase solidifies first to give a completely columnar structure.

Figs. 1 (c) and (d) (Plate IV) illustrate typical structures obtained in refined and standard ingots.

TABLE II.—Effect of Various Additions on the Grain-Size of Copper-7.5% Aluminium Alloy.

Ingot No.	Desired Compound	Lattice Misfit, %	Addition, % (nominal)	Macrostructure	Grain-size (average width, mm.)
1			Standard Ingot	Entirely columnar	4
2	CaB <sub>2</sub>	+13	0.05 Ca,* 0.02 B	"	3.5
3	CeB <sub>6</sub>	+13	0.05 Ce,* 0.02 B	"	3.5
	CeO <sub>2</sub>	+ 6		"	
4	CoB	+ 8	0.01 Co, 0.01 B	"	4
	Co <sub>2</sub> B	+15		"	
5	"	+15	0.10 Co, 0.10 B	"	4
6	Mo	-14	0.10 Mo	Fine columnar	1 $\frac{1}{2}$
	MoO	-18		Coarse equi-axial centre (1 $\frac{1}{2}$ in. dia.)	8 $\frac{1}{2}$
7	Nb	-10	0.10 Nb	"	...
	NbO	-14		"	
8	TiB <sub>2</sub>	-12	0.01 Ti, 0.01 B	Entirely columnar	4
	TiO	-18		"	
9	"	-18	0.10 Ti, 0.10 B	"	4
10	V	-17	0.10 V	Fine columnar	1 $\frac{1}{2}$
	VO	-17		Coarse equi-axial centre	7.5 $\frac{1}{2}$
11	W	-14		"	
	WO	-20	0.10 W	"	3.5
	W <sub>2</sub> O	-18		"	
12	ZrB <sub>2</sub>	-13	0.01 Zr, 0.01 B	Entirely columnar	4
	ZrO	-10		"	
13	"	-10	0.10 Zr, 0.10 B	"	4

\* Nominal addition increased to allow for high oxidation loss of these elements during addition.  $\frac{1}{2}$  Columnar.  $\frac{1}{2}$  Equi-axial.

TABLE III.—Eutectic Series : Laboratory Ingots.

Alloy No.	Composition : Al, %	Boron Addition, % (nominal)	Macrostructure	Average Grain-Size, mm.	
				Columnar (width)	Equi-axial
1	8.71	0.02	Fine equi-axial	...	0.5
2	8.63	Nil	Columnar	3	...
3	8.38	0.02	Fine equi-axial	...	0.5
4	8.34	Nil	Columnar	3	...
5	8.25	0.02	Fine equi-axial	...	0.5
6	8.04	0.02	Columnar	4	...

#### (b) Application to Commercial Billets

A similar series of tests was carried out on the eutectic series of alloys employing 700-lb. billets 10 in. in dia.  $\times$  45 in. long, cast by a semi-Durville process at the works of Messrs. N. C. Ashton, Ltd., Huddersfield.

The casting temperature was 1100° C., determined by immersion pyrometer immediately before pouring began. A nominal 0.02% boron was added to all except the standard billets. Transverse sections for macro-examination were taken at approximately 12 in. from both top and bottom of the billets. No detectable difference was noted between sections from the same billet.

The results obtained (Table IV) confirm those of the laboratory tests, although the effect of undercooling in the hypo-eutectic alloys was less marked. The billet containing 8.37% aluminium appeared to be a borderline case (Fig. 1 (e), Plate IV) having a fine equi-axial outer zone and a coarse equi-axial central core.

TABLE IV.—*Eutectic Series: Commercial Billets.*

Alloy No.	Composition: Al, %	Boron Addition, % (nominal)	Macrostructure	Average Grain-Size, mm.	
				Columnar (width)	Equi-axial
1	8.65	0.02	Fine equi-axial	...	2
2	8.55	Nil	Columnar	5	...
3	8.50	0.02	Fine equi-axial	...	2
4	8.44	Nil	Columnar	5	...
5	8.37	0.02	Fine equi-axial outside (2 in.); coarse centre	...	2, 10
6	8.28	0.02	Columnar	5	...

As undercooling is greatest at the mould/metal interface and decreases with distance inwards from that interface, it is to be expected that the proportion of the grain-refined zone would be greater in the smaller laboratory ingots than in the commercial billets.

## V.—HOT-WORKING BEHAVIOUR OF ALLOYS OF APPROXIMATELY EUTECTIC COMPOSITION

### 1. LABORATORY TESTS

Rectangular-section ingots  $1\frac{1}{2} \times 5 \times 8$  in. were cast under conditions similar to those described above. Two ingots were poured from each melt, 0.02% boron being added to the second billet. Three sections,  $\frac{1}{2} \times 1\frac{1}{2} \times 4$  in., were taken from the centre of each billet and subjected to the rolling procedure outlined in Table V. The temperature before rolling was 900° C.

TABLE V.—*Hot-Rolling Behaviour of Laboratory-Ingot Sections.*

Billet No.	Al, %	B, %	Structure	Reduction at 1st Pass, %		
				5	20	50
1	8.58	...	Entirely columnar	Satisfactory	Moderate cracking	Heavy cracking
2	8.53	0.02	Fine-grained, equi-axial	Satisfactory	Satisfactory	Satisfactory
3	8.42	...	Entirely columnar	Slight cracking	Heavy cracking	Heavy cracking
4	8.40	0.02	Fine-grained	Satisfactory	Satisfactory	Satisfactory

All the cracks appeared to originate at columnar grain boundaries.

### 2. COMMERCIAL TESTS

Attempts were made to forge sections from the commercial test billets, 12 in. long  $\times$  10 in. in dia., into slabs 3 in. thick. As far as possible, identical schedules were

followed. A temperature of 900° C. was employed for initial heating and for reheating the billets. Each of the grain-refined billets was forged satisfactorily, but an appreciable degree of cracking was evident on the standard billets. This cracking appeared at the beginning of the test and was again associated with columnar grain boundaries.

## VI.—DISCUSSION OF RESULTS

Cibula<sup>2</sup> has found that various carbides, borides, and nitrides of transition metals give grain refinement in certain copper-base alloys. Maximum refinement for tin bronzes was produced by ZrC, TiB<sub>2</sub>, or CoB, and for iron-free  $\beta$ -brass by ZrB<sub>2</sub>. All these combinations have proved ineffective for  $\alpha$  copper-aluminium alloys, even in cases where the lattice misfit was considerably less than with Cibula's alloys. This evidence does not appear to support the nucleation theory, but several possible reasons exist for such behaviour, the most probable of which are: (a) The nucleating compounds are not formed, i.e. they are unstable in the molten alloy, or one of the constituents of the compound(s) is removed by preferential combination with another element (possibly an impurity) in the alloy; (b) the concentration of the compound, if it is formed, is below its solubility limit in the molten alloy.

Although some measure of grain refinement is obtained in the  $\alpha$  alloys by the addition of molybdenum, niobium, vanadium, or tungsten, the effect produced is mainly one of reduction of columnar grain-size. This may be expected where the solubility of the nucleating element in the parent alloys is too small to allow of the formation of concentration gradients.<sup>3</sup>

Equi-axial structures can be expected only where the solubility of the grain-refining element in the parent alloy permits the formation of concentration gradients, or where these are produced by further additions.

Copper-aluminium alloys having aluminium contents ranging from just under the eutectic composition to 15% can be refined by the addition of boron.

The grain-refined structure obtained in alloys of approximately eutectic composition can be hot worked with less difficulty than the normal coarse columnar cast structure.

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# SOME OBSERVATIONS ON THE DEVELOPMENT OF FACE-CENTRED CUBIC ROLLING TEXTURES \*

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(Communication from the National Physical Laboratory)

## SYNOPSIS

Measurements of the development of the rolling textures of copper and  $\alpha$ -brass have been made, which indicate that, while the latter is consistent with deformation by slip on  $\{111\}$  planes, an additional mechanism is operative in copper.

## I.—INTRODUCTION

UNTIL comparatively recently, the sheet-rolling textures of face-centred cubic metals were considered to be  $\{110\}\langle 211 \rangle$ . However, the more accurate Geiger-Müller counter measurements of Hu, Sperry, and Beck,<sup>1</sup> Grewen and Wassermann,<sup>2</sup> and Smallman<sup>3</sup> have clearly established that, while the alloys such as  $\alpha$ -brass have the simple  $\{110\}\langle 211 \rangle$  texture, the texture of copper is quite different, being approximately  $\{123\}\langle 211 \rangle$ . The characteristic feature of this latter texture is a very strong maximum on the  $\{111\}$  pole figure about  $25^\circ$  towards the rolling direction from the centre.

Explanations of these differences based on the unequal hardening of active and latent slip planes in the alloys (the "overshoot" phenomenon) have been proposed by Bishop<sup>4</sup> and Calnan.<sup>5</sup> In addition, some consideration of how the solute atoms produce this unequal hardening has been given by Murphy and Calnan<sup>6</sup> and Smallman,<sup>3</sup> the latter showing the effect of concentration and atomic "misfit" of the solute on the textures obtained.

The foregoing experimental work has been concerned essentially with end-textures, that is to say, the textures reached after reduction of 90% or more. It was felt, however, that an attempt should be made to study the development of the textures with increasing reductions to see whether the semi-quantitative explanation proposed by Calnan was valid.

## II.—EXPERIMENTAL METHOD

The ideal way of describing sheet textures is by means of pole figures such as have already been obtained by Geiger-Müller counter methods for copper, aluminium,  $\alpha$ -brass, and various alloys by Hu, Sperry, and Beck,<sup>1</sup> Grewen and Wassermann,<sup>2</sup> and Smallman.<sup>3</sup> In view of the agreement between these results and since it was anticipated that examination of a considerable number of specimens would be necessary, the labour involved in the determination of complete pole figures was felt to be prohibitive, and it was therefore decided to restrict the

investigation to specific components of the textures. In particular these were:

(a) The  $\{111\}$  maxima at  $\pm 27^\circ$  from the rolling plane normal towards the rolling direction. These are the characteristic maxima of the copper texture.

(b) The  $\{110\}$  planes lying in the surface of the sheet. This corresponds to the main brass texture of  $\{110\}\langle 211 \rangle$ .

(c) The  $\{100\}$  planes in the surface of the sheet, corresponding to the copper recrystallization "cube" texture,  $\{100\}\langle 100 \rangle$ .

(d) The  $\{311\}$  planes in the surface of the sheet.

These last measurements were carried out at a later date after an unexpected behaviour of the  $\{110\}$  texture of copper had been found.

The measurements were made on a Geiger-Müller counter diffractometer (described by Coyle, Hale, and Wainwright<sup>7</sup>), using monochromatic Cu  $K\alpha_1$  radiation, the intensities being recorded on a scaler and mechanical register. The counter slit width was 59 minutes of arc to enable each diffraction line except one to be recorded with one setting of the counter. The brass  $\{110\}$  texture, however, gave a broad line which necessitated two further counter positions, one on each side of the main setting. The recorded intensities included the background intensity, but as this was a nearly constant additive term less than 5% of the main texture intensities, it did not affect the development of the texture as indicated by the total intensity. Depending on the glancing angle of the particular reflection, the area of the specimen irradiated varied between 30 and 60 mm.<sup>2</sup>.

For the  $\{110\}$ ,  $\{100\}$ , and  $\{311\}$  measurements, the specimen was set in the focusing position with the incident and diffracted beams inclined at the Bragg angle to the surface of the sheet. For the irrational  $\{111\}$  texture corresponding to planes tilted  $27^\circ$  from the rolling plane normal towards the rolling direction, the sheet was set with the rolling direction horizontal and the horizontal X-ray beam incident at the Bragg angle plus  $27^\circ$ . Preliminary measurements were made to establish the peak positions of this irrational texture, and, to guard against asymmetry in the sheet, the two

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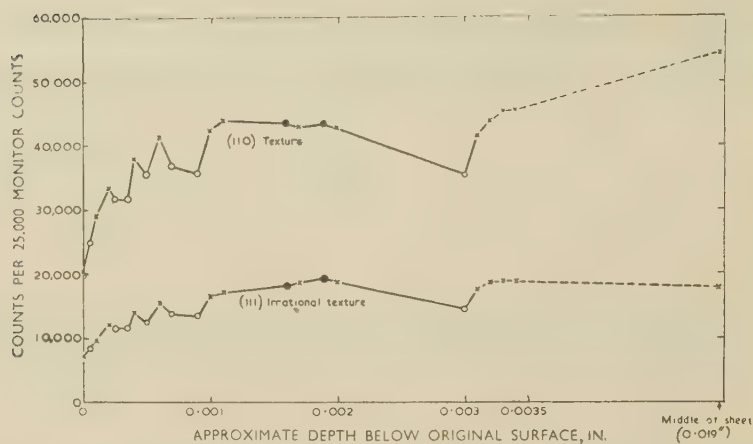


FIG. 1.—Effect of Surface Preparation on Texture Measurements on Copper after 85% Reduction.

KEY.  
 × After etching.      o After rubbing on 00 emery paper.      • After rubbing followed by etching.

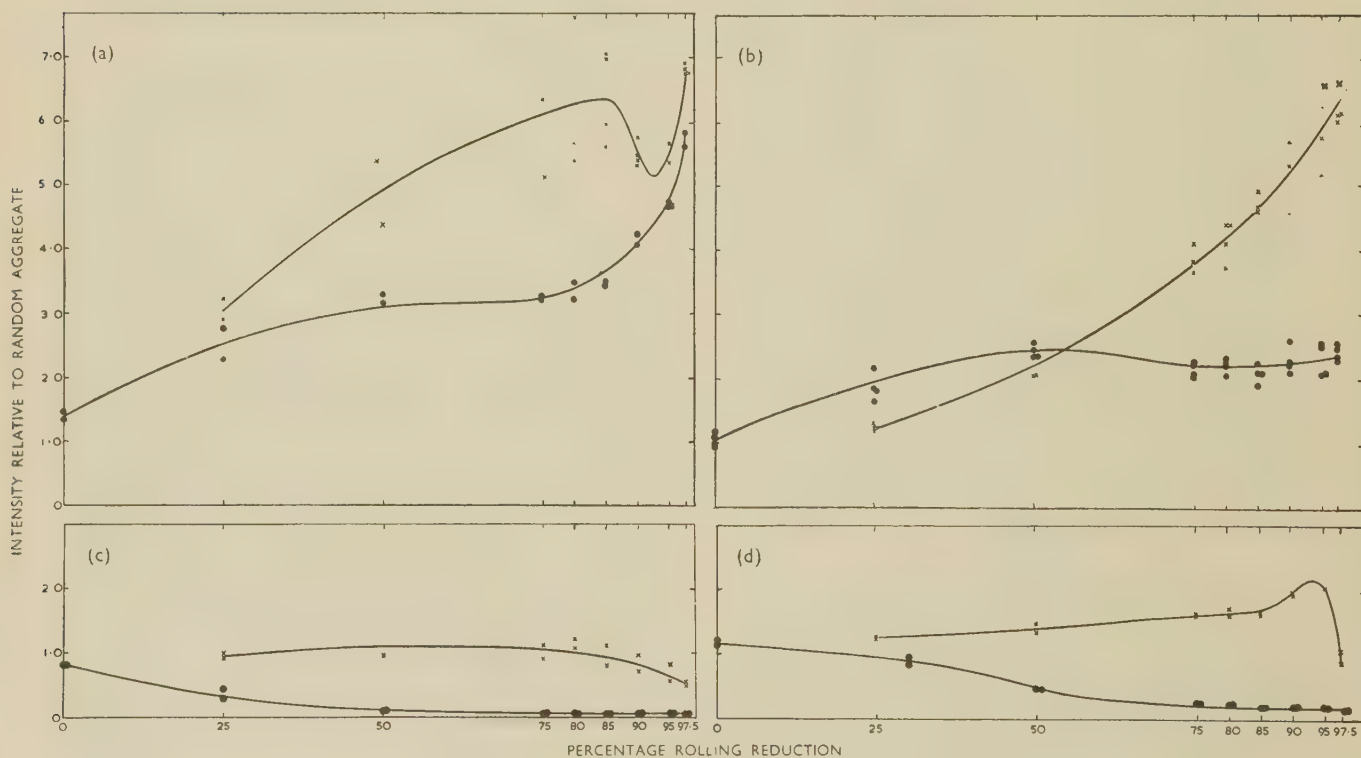


FIG. 2.—Textures in Cold-Rolled Copper and Brass.  
 (a) (110) texture.      (b) (111) irrational texture.      (c) (100) texture.      (d) (311) texture.

KEY.  
 × Copper.      • Brass.



peaks,  $27^\circ$  towards and away from the rolling direction, were measured.

Special attention was paid to the preparation of the specimen, since attempts to compare intensities on different specimens were vastly influenced by the surface condition of the material. This does not matter so much when an end-texture is being determined on a complete pole figure, since the intensities at different parts of the pole figure might be assumed to be scaled down in proportion, but it is vitally important if the amounts of a particular texture in different specimens are being compared. The matter is complicated by the desirability of measuring the true inside texture, i.e. the middle of the sheet, which involves removing considerable quantities of material, particularly on the low-reduction specimens. This may be done by severe etching or abrasion, but both these methods are open to objection. The former produces a fibrous surface, presumably due to preferential attack, which could not be trusted for representative measurements and must therefore be removed by further polishing and etching. Alternatively, severe abrasion would appear to be unwise on a material in a state near spontaneous recrystallization, and in any case subsequent etching would be required to remove the abraded surface. In view of the variations which successive abrasion and etching can produce, as illustrated in Fig. 1 by the results on one specimen, any method involving both abrasion and etching is suspect owing to the difficulty of ensuring that such a procedure has a standard effect. Accordingly, a more easily standardized procedure had to be found. Electrolytic polishing proved to be unsatisfactory, as the amount of copper removed was small if the current was low enough to preserve a good surface.

Taking the measurements in Fig. 1 corresponding to the etched condition as more nearly approaching the true intensity of texture, it will be seen that there is a rapid variation in the first 0.001 in. below the surface of the sheet and thereafter a very slow variation. This gives some justification for accepting the values corresponding to 0.001 in. below the surface as the inside texture of the sheet so long as the preparation to reach this depth is accurately controlled. The procedure finally adopted, which satisfies this condition and at the same time retains a suitably smooth surface for the measurements, consisted simply in etching in 50% nitric acid until 0.001 in. had been removed. The reproducibility of the results on brass specimens of a given reduction, as shown in Fig. 2 (a)–(d), gives confidence in the reliability of this method of preparation.

The measurements were made on O.F.H.C. copper and 70 : 30 brass, cold rolled and annealed to give grain-sizes of approximately 0.1 mm. Analysis of the copper showed the following impurities (%): Ag 0.002; Pb 0.00035; Fe 0.0001; Sb 0.0003; Ni 0.0002; Te  $>0.003$ ; Sn  $<0.005$ ; Mn, Si, As, Zn  $<0.002$ ; Co, Bi  $<0.0001$ ; and 0.006 loss in hydrogen. The material was cold rolled with reverse passes of 0.005 in. up to about 65% reduction of thickness and subsequently with reverse passes of 0.0025 in. Samples were cut from the sheets at thicknesses corresponding to percentage reductions of 25, 50, 75, 80, 85, 90, 95, and 97.5. Two specimens of each material at each reduction were examined initially, followed by an additional two in the case of copper for reductions above 75%.

### III.—EXPERIMENTAL RESULTS

The development of the textures in copper and  $\alpha$ -brass relative to randomly oriented compacts of annealed filings are shown in Fig. 2 (a)–(d). The results on all the specimens are given to illustrate the variation between individual measurements. The intensities from the copper before rolling were subject to large variation due to grain-size, and therefore are omitted from the results. From 25% reduction onwards, the rolling reduced the grain-size sufficiently for this effect to be small. It will be seen that the brass results are much more consistent than the copper values, of which the {110} texture shows the greatest scatter, particularly between reductions of 50 and 95%. The reproducibility of the intensity measurements on a given specimen, however, was very much better; repeat values on twelve specimens, including re-setting in the diffractometer, showed a mean variation of about 2%.

In detail, the brass behaves in accordance with the slip predictions in respect of the increase of the {110} texture and the decrease of the {100} and {311} components. The slight initial rise of the {111} irrational texture is unexplained unless it corresponds to orientations moving on their way towards the {110} texture. For the copper up to 85% reduction in accordance with the slip predictions the {110} increases and the {100} persists much more than in brass. The more important feature in the copper, however, is the anomaly at 90 and 95% reduction. The results here indicate that while the irrational texture builds up continuously with increasing deformation the {110} component dips to a minimum and then climbs again at 97.5% reduction. The objection that these intensity measurements do not correspond to texture differences was considered; it is possible that the diminution of the {110} is due to extra line-broadening or tailing of the lines. Side counts and chart records revealed no significant effect, however.

Alternatively, it is conceivable that some extinction effect is occurring at these particular reductions. This should be evident from the ratio of {220} and {440} reflections. Measurements for all the reductions showed no anomaly at 90% and, in fact, the extinction acts if anything in the opposite direction. It is thus considered to be a true texture effect. In this case, it is completely at variance with all theories based on {111} slip rotations, for no one has ever suggested that grains once in the stable {110}<211> end-point could rotate by slip away from this orientation. In particular, it demands an additional mechanism at work in copper, and since this mechanism is likely to influence the final texture, an explanation based solely on overshoot in brass and its absence in copper is correspondingly insufficient.

There is no evidence that the irrational texture increases more rapidly at the point where the {110} decreases, that is to say, there is no direct transfer of orientation. The {311} texture, however, does behave rather oddly. Firstly, on a slip basis there is no reason why it should increase even though it might persist, and secondly, there is a small additional increase coinciding with the {110} decrease followed by a sudden decrease as the {110} rises again.

These observations may be interpreted in terms of a variety of additional mechanisms with varying degrees of success, but this can only be speculation. At the

moment it does not appear possible to distinguish with certainty between the several explanations which might be advanced, but it is hoped that further experiments will resolve this difficulty.

#### IV.—CONCLUSIONS

It has been shown that, while brass conforms with a slip mechanism to the very highest deformations, the  $\{110\}$  texture in copper, and to a lesser extent the  $\{311\}$  texture, betrays a mechanism which is contrary to  $\{111\}$  slip rotations. It is concluded that an explanation of the texture differences based on  $\{111\}$  slip with the occurrence of overshoot in brass and its absence in copper is therefore insufficient.

#### ACKNOWLEDGEMENT

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# OBSERVATIONS ON GRAIN-BOUNDARY MIGRATION 1714 IN ALUMINIUM BICRYSTALS \*

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## SYNOPSIS

The experimental technique suggested by Dunn, Daniels, and Bolton (*Trans. Amer. Inst. Min. Met. Eng.*, 1949, **185**, 708) for studying grain-boundary migration is shown to have considerable merit. The rates of grain-boundary migration have been measured at temperatures of 560°, 600° and 640° C. for strain-free bicrystals of aluminium having orientation differences of 55° and 85° about  $\langle 110 \rangle$ . Activation energies of 43 and 20 kg.cal./g.-atom, respectively, were calculated from these data.

## I.—INTRODUCTION

THE present investigation was initiated to determine whether a method suggested by Dunn and his co-workers<sup>1</sup> is suitable for studying the rate of grain-boundary migration in strain-free aluminium bicrystals as a function of orientation difference and temperature. The type of specimen suggested by Dunn *et al.* is shown in Fig. 1, in which the radius of curvature of the moving

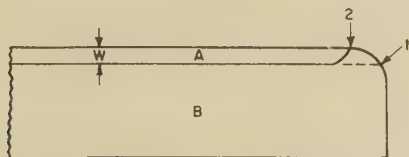


FIG. 1.—Schematic Diagram of Bicrystal for Studying Grain-Boundary Migration, Showing Growth of Crystal *B* at the Expense of Crystal *A*. Grain-boundary movement is depicted from position at 1 to position at 2.

boundary is kept constant. The driving energy for the boundary migration is  $\gamma/W$ , where  $\gamma$  is the interfacial energy per unit area of the straight part of the boundary and  $W$  is the width of the narrow crystal (*A*) of the bicrystal. The width,  $W$ , was maintained constant (0.9 mm.) in all the specimens studied in order to measure the effect of orientation difference between crystals *A* and *B*. Assuming a boundary energy of 500 ergs/cm.<sup>2</sup>, the driving energy for boundary migration here is about 0.0013 cal./g.-atom.

## II.—EXPERIMENTAL PROCEDURE

Bicrystals were grown in argon atmosphere by “seed-ing” and controlled-solidification techniques<sup>2</sup> from aluminium of 99.997% purity. The orientation differences were 55° and 85° about a  $\langle 110 \rangle$  specimen axis direction, parallel to the growth direction, obtained by rotating one crystal of a bicrystal about a  $\langle 110 \rangle$  direction while the other crystal remained fixed. The orientation of the straight portion of the grain-boundary plane with respect to the narrow crystal being consumed was within 4° of

a  $\{511\}$  plane for all specimens with  $\theta = 55^\circ$ , and within 3° of a  $\{111\}$  plane for all specimens with  $\theta = 85^\circ$ .<sup>3</sup> The orientation differences  $\theta$  were determined by the X-ray back-reflection Laue method. The accuracy of the orientation determination was only  $\pm 2^\circ$  because of the lineage or macro-mosaic boundaries present in all the bicrystals.

The specimens were prepared in the shape illustrated in Fig. 1 by cutting with a jeweller's saw and wet polishing to 400 emery paper. The specimens were deeply etched in *aqua regia*, electropolished in a 2 : 1 solution of methyl alcohol and concentrated nitric acid for periods up to  $\frac{1}{2}$  hr. at a current density of 10 amp./dm.<sup>2</sup> and then chemically polished for periods up to 15 min. with Alcoa R-5 bright dip solution. This was followed by an anneal at 500° C. for 20 hr. in order to remove possible strains due to specimen preparation. Interrupted isothermal anneals were then conducted at temperatures of 640°, 600°, and 560° C. in an argon atmosphere by inserting the chemically polished specimens into the furnace at temperature. The amount of grain-boundary movement was determined by microscopic measurement at room temperature.

## III.—EXPERIMENTAL RESULTS

It was generally found that the grain-boundary movement in the initial stages of isothermal annealing was relatively slow, i.e. less than 0.2 mm./hr. During this initial slow stage, the movement was irregular in the sense that the distance traversed by the boundary was not identical on both the top and bottom surfaces of the specimen. In some cases, the boundary appeared to have difficulty in breaking away from the tip of the specimen (at arrow 1 in Fig. 1). No correlation was found in the rate of movement during this initial stage with either temperature of anneal or orientation difference. However, when the boundary reached the approximate position where the curvature of the narrow crystal ended (near arrow 2, Fig. 1), a more rapid and uniform boundary motion occurred, resulting in the disappearance of the narrow crystal. The orientation of the specimen was now entirely that of crystal *B*, as determined by etch-

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pits and X-ray back-reflection photographs. The rapid, uniform migration is believed to be typical of the specimen, i.e. dependent on the driving energy for grain-boundary migration.

Results obtained for the uniform boundary migration as a function of isothermal annealing at 640°, 600°, and

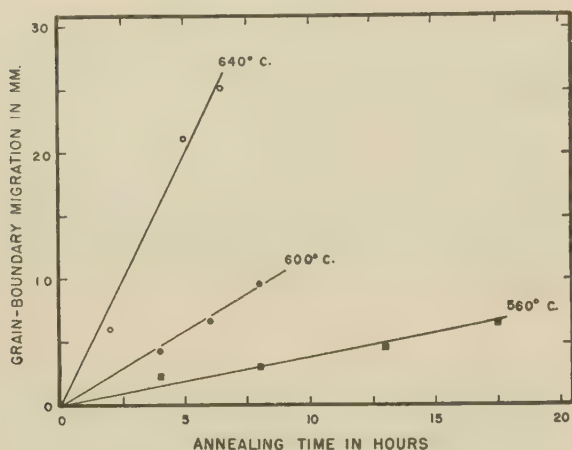


FIG. 2.—Grain-Boundary Migration (in mm.) versus Annealing Time (in hr.) at 640°, 600°, and 560°C. for Aluminium Bicrystals with  $\theta = 55^\circ$  about  $\langle 110 \rangle$ .

560°C. are shown in Fig. 2 for bicrystals with  $\theta = 55^\circ$  about  $\langle 110 \rangle$ , and in Fig. 3 for  $\theta = 85^\circ$  about  $\langle 110 \rangle$ . The zero points in the plots of Figs. 2 and 3 were taken when the relatively rapid, uniform migration began.

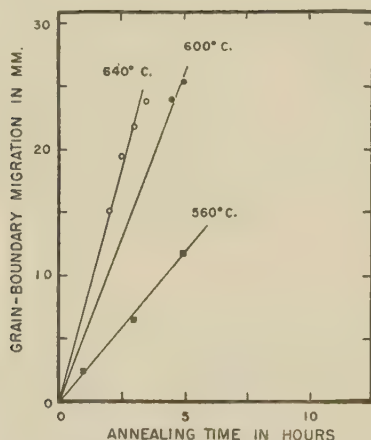


FIG. 3.—Grain-Boundary Migration (in mm.) versus Annealing Time (in hr.) at 640°, 600°, and 560°C. for Aluminium Bicrystals with  $\theta = 85^\circ$  about  $\langle 110 \rangle$ .

The relationship between the log rate of boundary migration and the reciprocal of the absolute annealing temperature is given in Fig. 4. The uncertainty in the resulting activation energies ( $Q$ ) is estimated to be  $\pm 5$  kg.cal./g.-atom. It appears that a boundary separating crystals with a misorientation of  $85^\circ$  about

$\langle 110 \rangle$  migrates at a faster rate and with a smaller activation energy than a boundary with  $\theta = 55^\circ$  about  $\langle 110 \rangle$ .

The free energy of activation for boundary migration ( $\Delta F_A$ ) at 600°C. was calculated to be 15 and 13 kg.cal./g.-atom from the present data for orientation relationships of  $55^\circ$  and  $85^\circ$  about  $\langle 110 \rangle$ , respectively. These calculations were carried out in a manner described by Turnbull,<sup>4</sup> and assuming a boundary thickness of  $2 \times 10^{-8}$  cm. and a boundary energy of 500 ergs/cm.<sup>2</sup>

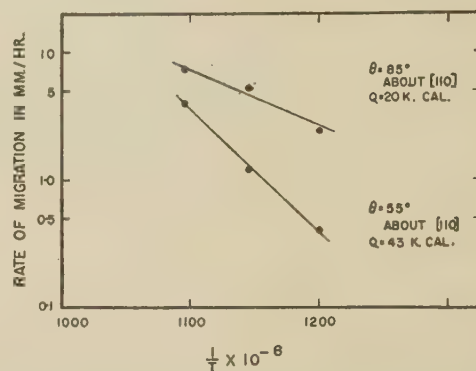


FIG. 4.—Relationship between the Log Rate of Boundary Migration and the Reciprocal of the Absolute Annealing Temperature for  $\theta = 55^\circ$  and  $85^\circ$  about  $\langle 110 \rangle$ .

Turnbull has calculated a value of  $19.7 \pm 2$  kg.cal./g.-atom for normal grain growth in aluminium in the temperature range of 400°–500°C. from the experimental data of Beck *et al.*<sup>5</sup>

#### IV.—CONCLUSION

The experiments reported herein have shown that the method of studying grain-boundary migration advanced by Dunn and his co-workers should be of considerable value in further studies of the influence of orientation difference on boundary mobility. It should also be possible, using similar techniques, to investigate the effects of sub-structures and the orientation of the grain boundary itself upon the movement of grain boundaries.

#### ACKNOWLEDGEMENT

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# THE ATTACK OF UNSTRESSED METALS BY LIQUID MERCURY\*

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(Communication from the Staff of the Research Laboratories of The General Electric Co., Ltd., Wembley)

## SYNOPSIS

The saturated solubilities and weight losses at room temperature of most of the metallic elements in static liquid mercury have been determined, usually to 0.001%, by chemical analysis of the solutions and by weighing the specimens. The solubilities show a periodic relationship with the atomic number, and there are indications that this can be related to the inner electronic shell structure. In general, the solubilities of the B sub-group elements exceed those of the true metals, while of this latter group the transition metals show the lowest values.

When attack occurs, it involves wetting, surface amalgamation, solution, and occasionally combination and intergranular penetration. The effect of oxide films has been investigated.

The tests were conducted as far as possible in the absence of air, since oxidation brought some metals out of solution in mercury, leading to ambiguities. Exposure to air can result, for example, in a form of mass transfer.

No significant changes take place in the mechanical properties of iron, molybdenum, some steels, and nickel alloys after 2000 hr. in mercury at 500° C. Nickel suffers a decrease in maximum stress, yield stress, and elongation of about 50%.

Severe cavitation erosion of metals and alloys, normally resistant to mercury, occurs at room temperature on the application of 30 kc./s. ultrasonic vibrations.

## I.—INTRODUCTION

THE possibility of using liquid metals as coolants in nuclear reactors has stimulated studies of the attack of solid metals by liquid metals. The work described here forms part of such a programme and has yielded some results of general interest.

An experimental survey of the saturated solubility of most of the metallic elements, bright-annealed and unstressed, in static liquid mercury at room temperature, and of the attack upon them at room temperature and 500° C., has been carried out by the appropriate use of some or all of the following techniques: measurement of the change in weight of the specimens, chemical analysis of the solutions, microscopic examination of etched sections of the specimens, and X-ray examination of products of attack. The metals were exposed to mercury in the absence of air to avoid complications and ambiguities in the results. The presence of air probably accounts for many of the discrepancies which appear in the literature.

The attack on bright-annealed and unstressed commercial nickel, Inconel, Nimonic 75, 50:50 nickel-iron, 20% nickel-25% chromium steel, 8% nickel-18% chromium steel (Firth's F.D.P.), 3.5% silicon-8% chromium valve steel, mild steel, iron, molybdenum, and tungsten, in static liquid mercury at 300° and 500° C. for up to 2000 hr., was also studied. In addition to the four techniques listed, the extent of the attack was further determined by the variations in maximum stress, yield stress, hardness, and percentage elongation. For this reason these mechanical-test specimens were

made as flat tensile-test specimens for use with a Hounsfield tensometer.

The effect on mercury attack of removing oxide films, adsorbed gas, and water-vapour layers from the surfaces of some metals and alloys was examined. Trials under dynamic liquid-mercury conditions at room temperature were carried out by imposing 30 kc./s. ultrasonic vibrations on some materials.

This work was undertaken for the Atomic Energy Research Establishment, and a detailed account of part of it is given in a report<sup>1</sup> issued by the A.E.R.E. and the Research Laboratories of The General Electric Co., Ltd.

## II.—EXPERIMENTAL TECHNIQUES

### 1. SPECIMENS AND MERCURY

Where possible, the metallic elements were obtained as flat sheets 0.006–0.040 in. thick, as this form gave the maximum area of contact between the specimens and the mercury for a given weight of specimen, consistent with ease of handling and accurate weighing. Most of the samples were obtained from Johnson, Matthey and Co., Ltd., and their purities ranged from 99+% to 99.99%, except for magnesium, calcium, and chromium, the purities of which were 98%, "Commercial Grade", and 98–99%, respectively. The beryllium, potassium, arsenic, strontium, barium, tantalum, and thorium samples were of high-grade material, but the exact purities are unknown.

The metal and alloy specimens subsequently sub-

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mitted to mechanical test ranged in thickness from 0.013 to 0.036 in. They were blanked from sheet material to the usual form for tensile tests. An exception was made with the tungsten specimens, which were of 0.02-in.-dia. wire and about 8 in. long.

The various specimens were degreased whenever practicable, and bright-annealed in a hydrogen or nitrogen atmosphere or under high-vacuum conditions of about  $10^{-5}$  mm. Hg. The annealing temperatures chosen led to recrystallization of most of the metals, with the exception of molybdenum and tungsten, for which the lattice strains only were removed. Where the appropriate annealing temperatures were not found in the literature, e.g. for manganese, germanium, arsenic, strontium, barium, and thallium, it was decided to treat each metal at a temperature equal to two-thirds of its melting-point temperature.

Bright-annealing treatments requiring temperatures above 500° C. were carried out in the appropriate atmosphere in silica-tube furnaces, except for temperatures above 1200° C., where mullite (72 alumina: 28 silica) tube furnaces were used. After bright-annealing, the surfaces of the specimens were as clean and as free from oxide films as could be expected without recourse to extremely elaborate methods. The specimens were then stored in a hot cupboard at about 85° C. until they were weighed and immersed in the mercury. Handling with gloved hands or tweezers minimized the possibility of surface contamination. The annealing treatments below 500° C. were carried out under high-vacuum conditions on weighed specimens in the "Wembley W1" hard-glass containers used for the subsequent tests, and the mercury was distilled directly into the vessels after they had cooled to room temperature.

The mercury used in these experiments was purchased as 99.997 wt.-% pure, and was submitted to a cleaning, filtering, drying, and distilling process before use.

## 2. CONTAINERS AND VACUUM TECHNIQUES

The prepared specimens were inserted in cylindrical W1 glass containers ranging from approximately  $1\frac{1}{2}$  in. dia.  $\times$  7 in. long to  $\frac{1}{2}$  in. dia.  $\times$   $1\frac{1}{2}$  in. long, to suit the varying specimen sizes. Before use, the containers were washed with chromic acid solution and distilled water, and then dried. Each container had a relatively long thin neck, constricted to facilitate subsequent sealing under vacuum conditions. The neck ensured that each specimen, which would otherwise float, was trapped below the mercury level, and that there was ample room for expansion of the mercury at the higher temperatures. Hard glass was used as being convenient for high-vacuum techniques and offering the minimum possibility of interaction between itself, the mercury, and the specimens. Further, it is suitable for tests at 500° C., as negligible diffusion of air and other gases through the glass would be expected at that temperature.

For the tests on the variations in mechanical properties after exposure to mercury at 300° C., three or four specimens of each material were assembled on short lengths of W1 glass tubing. Each assembly of these mechanical-test specimens was inserted into a glass container, the base of which was then drawn off. When the glass had cooled, mercury was poured through the

neck, the vessel evacuated to a pressure of a few mm. Hg, and sealed off. The vessels were then placed in a stand inside a furnace thermostatically controlled to  $300^{\circ} \pm 5^{\circ}$  C.

The mechanical-test specimens and the mercury for the 500° C. tests were held in special containers of 8% nickel-18% chromium steel, since the glass containers could not have withstood the mercury-vapour pressure of about 8 atm. corresponding to this temperature. This steel is not subject to oxidation at 500° C. The lid of the vessel formed a vacuum-tight seal by pressure on a copper sealing ring. The air was not removed in these experiments. The vessels were placed in furnaces thermostatically controlled to  $500^{\circ} \pm 5^{\circ}$  C. The interiors of the vessels and the inner faces of the lids were cleaned and sand-blasted on every occasion before use.

The solubility experiments were carried out on pieces of the metallic elements not larger than  $\frac{1}{2} \times \frac{1}{2}$  in., so that small W1 glass vessels could be used. Each vessel with its specimen was sealed to a high-vacuum system, evacuated by a three-stage mercury-diffusion pump backed by a mechanical pumping system, and to a still containing mercury. Pressures were measured by McLeod and Pirani gauges.

The mercury was distilled into each vessel, which was then sealed off under high vacuum and maintained either at room temperature or at 500° C. for the desired time. For the tests at 500° C. the glass vessels were small enough to be placed in the steel vessels already described, together with sufficient mercury to ensure pressure equality inside and outside the glass vessels to prevent their bursting.

Owing to the relatively high mercury-vapour pressure in the experiments at 500° C., and to the likelihood of mercury-vapour attack on the copper sealing rings, especially during long runs, the possibility of the escape of mercury vapour had to be considered. Thus, periodical tests were made on each vessel containing mercury, by removing it from the furnace and checking the weight. This was done as rapidly as possible to avoid cooling of the vessels, as this in itself could cause leaks to develop, owing to the differential expansion of the copper and the steel.

In addition, a sensitive test for the presence of mercury vapour in the neighbourhood of the ovens was set up. This consisted essentially of a low-pressure mercury-vapour quartz tubular lamp radiating across the top of the oven on to a fluorescent screen. Even slight amounts of mercury vapour in the air above the oven appeared as dark billowing clouds on the screen, owing to the resonance absorption by the mercury-vapour atoms of radiation of wave-length 2537 Å.

## 3. ANALYTICAL TECHNIQUES

The techniques used to investigate the attack and the solubility of the various metallic elements, and the changes in the mechanical properties of some metals were:

(i) Determination of the change in weight of the specimens after total immersion in a known weight of mercury for times ranging from 0.3 to 2661 hr. Long time intervals were mainly used to ensure saturation. This gave the weight percentage change.



(ii) Filtration of the solutions, after removing the specimens, through a Pyrex sintered-glass crucible of pore size 90–150  $\mu$ . Determination of the metal content both in the filtrate and the residue by chemical analysis. The former gave the weight percentage solubility, and their sum the weight percentage loss.

(iii) Microscopic examination of etched sections of the specimens.

(iv) X-ray examination of products of attack in some cases.

(v) Determination of changes in maximum stress,

Transverse and longitudinal sections of representative samples of all the materials subjected to mechanical tests, and of all those metallic elements which formed surface products of attack were taken. These were etched, examined under the microscope, and photographed.

To distinguish between mechanical variations due to exposure to the mercury at 500° C. and those due to the prolonged soaking at this temperature, control experiments were carried out at  $500 \pm 5^\circ$  C. under high-vacuum conditions.

	True Metals														B Sub-Groups					
	Transition Metals																			
	I	II	III	IV	V	VI	VII	VIII	I	II	III	IV	V	VI						
2	<sup>3</sup> Li 0.023(2) 0.660(2)	<sup>4</sup> Be <0.001(1) <0.022(1)																		
3	<sup>11</sup> Na 0.101(2) 0.880(2)	<sup>12</sup> Mg <0.001(3) <0.008(3)													<sup>13</sup> Al <0.001(2) <0.007(2)	<sup>14</sup> Si <0.001(1) <0.007(1)				
4	<sup>19</sup> K 0.006(1) 0.031(1)	<sup>20</sup> Ca <0.001(1) <0.005(1)	<sup>21</sup> Sc	<sup>22</sup> Ti <0.001(1) <0.004(1)	<sup>23</sup> V 0.041(3) 0.161(3)	<sup>24</sup> Cr 0.002(2) 0.007(2)	<sup>25</sup> Mn <0.002(1) <0.007(1)	<sup>26</sup> Fe <0.001(2) <0.004(2)	<sup>27</sup> Co <0.001(2) <0.003(2)	<sup>28</sup> Ni 0.002(3) 0.007(3)	<sup>29</sup> Cu 0.007(5) 0.022(5)	<sup>30</sup> Zn 1.333(2) 4.07(2)	<sup>31</sup> Ga	<sup>32</sup> Ge <0.001(1) <0.003(1)	<sup>33</sup> As 0.244(3) 0.646(3)	<sup>34</sup> Se				
5	<sup>37</sup> Rb 0.006(1) 0.014(1)	<sup>38</sup> Sr	<sup>39</sup> Y	<sup>40</sup> Zr 0.003(1) 0.007(1)	<sup>41</sup> Nb <0.001(1) <0.002(1)	<sup>42</sup> Mo <0.001(1) <0.002(1)	<sup>43</sup> Tc	<sup>44</sup> Ru 0.353(2) 0.694(2)	<sup>45</sup> Rh 0.16(2) 0.311(2)	<sup>46</sup> Pd 0.006 0.012(2)	<sup>47</sup> Ag 0.039(4) 0.072(4)	<sup>48</sup> Cd 5.29(2) 9.41(2)	<sup>49</sup> In >1.600(1) >2.800(1)	<sup>50</sup> Sn 0.152(2) 0.256(2)	<sup>51</sup> Sb 0.020(1) 0.033(1)	<sup>52</sup> T				
6	<sup>55</sup> Cs	<sup>56</sup> Ba <0.001(2) <0.001(2)	<sup>57</sup> La																	
				<sup>72</sup> Hf	<sup>73</sup> Ta 0.010(1) 0.011(1)	<sup>74</sup> W <0.001(1) <0.001(1)	<sup>75</sup> Re	<sup>76</sup> Os	<sup>77</sup> Ir <0.001(1) <0.001(1)	<sup>78</sup> Pt 0.002(2) 0.002(2)	<sup>79</sup> Au 0.126(4) 0.128(4)	<sup>80</sup> Hg $\infty$ $\infty$	<sup>81</sup> Tl >13.4(1) >13.1(1)	<sup>82</sup> Pb 1.083(3) 1.06(3)	<sup>83</sup> Bi 0.87(2) 0.835(2)					
7		<sup>88</sup> Ra	<sup>89</sup> Ac	<sup>90</sup> Th 0.008(2) 0.007(2)	<sup>91</sup> Pa	<sup>92</sup> U														

The upper figure in each block refers to the weight per cent.; the lower figure in each block refers to the atomic per cent.

FIG. 1.—Periodic Table Giving the Percentage Solubility of the Metallic Elements in Liquid Mercury at Room Temperature.

yield stress, percentage elongation, and hardness after total immersion for 500, 1000, and 2000 hr.

The smallest observable weight percentage loss by method (i) was of the order of 0.0002–0.001%, since the specimens were weighed to an accuracy of  $\pm 0.0001$  g. before and after each test run, and about 10–50 g. mercury were used in each test. When wetting occurred, the specimens were baked at temperatures up to 500° C. for about  $\frac{1}{2}$  hr. under high vacuum to remove residual mercury before weighing or sectioning. However, since the method involved the detection of the small difference between two relatively large quantities, the limit of accuracy was unlikely to exceed 0.001%.

The sensitivity of method (ii) varied according to the nature of the metal and the amount of mercury from the test available for analysis. Generally, the lower limit adopted involved the determination of 0.0005 g. of metal in 25–50 g. of mercury, corresponding to a weight percentage solubility of 0.002–0.001%. Chemical methods of greater sensitivity would have involved elaborations not thought justified for this general survey. Methods (i) and (ii) were thus of similar sensitivity. As method (i) was the simpler, this was carried out wherever possible as a preliminary test; chemical analysis was employed only where the weight percentage loss exceeded 0.001%, or where the weight-loss method could not be applied.

### III.—EXPERIMENTAL RESULTS

#### 1. SOLUBILITY AND WEIGHT LOSS OF THE METALLIC ELEMENTS

The results for the solubility of the metallic elements at room temperature are summarized in periodic-table form in Fig. 1. In each block, the upper figure is the weight percentage solubility and the lower figure the corresponding atomic percentage. The figures in parentheses record the number of tests carried out on each element, the value quoted being the average of these; thus the figures in parentheses indicate the "weighting" of the results.

The solubility at room temperature is given by chemical analysis of the filtrate after the runs at 500° C. as well as after the room-temperature runs. This is justified, since precipitation of excess solute would have occurred on dropping from 500° C. to room temperature, especially in the presence of excess solid metal acting as nuclei to initiate the precipitation.

The weight percentage loss at room temperature in general exceeded the weight percentage solubility, while the weight percentage loss at 500° C. exceeded that at room temperature, as would be expected. In many cases the attack on the samples, or oxidation on exposure to air, was so extensive that the samples in their original forms disappeared, rendering their weight-loss measure-

ments an unsatisfactory guide to the magnitude of the attack. Occasionally a negative weight loss occurred, implying that a tenacious product of attack had built up on the specimen, so increasing its weight.

The symbols used in Figs. 1 and 2 have the following connotations:

- < : Where no dissolved material or loss of weight was detected, the solubility is quoted as <0.001%.
- > : Solubilities quoted as > a certain value imply that the sample dissolved completely, resulting in a solution which was probably unsaturated.

## 2. RATES OF ATTACK ON THE MECHANICAL-TEST SPECIMENS

The rates of attack for commercial nickel, Inconel, Nimonic 75, and 50 : 50 nickel-iron are given in Table I in terms of milligrammes weight lost per square decimetre per day. The values at 500° C., except those for nickel-iron, correspond to losses ranging from 0.005 to 0.20

TABLE I.—Rates of Attack of Unstressed Materials Immersed in Liquid Mercury at 300° and 500° C.

Material	Temperature, °C.	Rate of Attack, mg./dm. <sup>2</sup> /day *				
		After 100 hr.	After 145 hr.	After 500 hr.	After 1000 hr.	After 2000 hr.
Commercial Nickel (<99.35% Ni)	300 500	... 444	... 259	1 23	3 19	2 7
Inconel (80 Ni/14 Cr/6 Fe)	500	...	...	3	2	4-11
Nimonic 75 (75 Ni/20 Cr/5 Fe)	500	...	...	15	3-23	6
50 : 50 Nickel-Iron	300 500	... ...	... ...	1 0	2 0	0 0

\* Each value in the table is the average of 3-4 separate determinations, and is given to the nearest unit.

wt.-%. No attack was detected with the other materials, 20% nickel-25% chromium steel, 8% nickel-18% chromium steel, 3.5% silicon-8% chromium steel, mild steel, iron, molybdenum, or tungsten, after 500, 1000, and 2000 hr. in mercury, either at 300° or 500° C. In each test an assembly of 3-4 separate specimens of each type was used. For comparison purposes, rough generalizations<sup>2</sup> are given in Table II.

TABLE II.—Rates of Attack: Comparison Data (after McKay and Worthington<sup>2</sup>).

Rate of Attack, mg./dm. <sup>2</sup> /day	Remarks
0	Low limit of measurement and represents "no practical attack".
1-10	Represents very slight attack.
10-100	Attack must be taken into consideration.
Near 100	Attack may be serious.
100-500	Attack is serious.
>500	Usually represents failure.

The rates of attack at 300° C. for commercial nickel, and at 300° and 500° C. for 50 : 50 nickel-iron are "very slight". For commercial nickel, Inconel, and Nimonic

75 at 500° C., the rates from 500 hr. onwards represent attack which "must be taken into consideration". However, two short-term tests on nickel of about 100 hours' duration gave rates of attack of several hundreds of mg./dm.<sup>2</sup>/day, which are "serious". Although these variations in the rates of attack for nickel may indicate a saturation effect, since they decrease with time, a "critical temperature" may exist at about 500° C. It should be noted that the commercial nickel, Inconel, and Nimonic 75 are all nickel-containing alloys with 99.35% minimum, 80%, and 75% nickel, respectively. None of the other materials tested gave any indication of weight loss. In fact, a slight increase in weight was experienced at 500° C. with all of them except tungsten wire. This increase was most noticeable with mild steel, iron, silicon-chromium steel, and 20% nickel-25% chromium steel, being less with molybdenum and nickel-iron, and very small indeed with 8% nickel-18% chromium steel. Thus, it was probably due to oxidation of these materials at 500° C. from air either entrapped or dissolved in the mercury, as no attempt was made in these experiments to remove the air. It is not likely that this weight increase masked any significant attack, since microscopic examination of specimen sections and tests on their mechanical properties confirmed the absence of attack. If development of oxide films was responsible for the weight increase, then enhanced protection of the specimens might be expected, especially with the chromium steels which form thin, stable, continuous, and passive oxide films.

The commercial nickel specimens were partially wetted by the liquid mercury at 300° C. and completely wetted after each run at 500° C. The Inconel and Nimonic 75 specimens were only partially wetted after each run at 500° C. Of the other materials tested, traces of patchy wetting occurred occasionally with nickel-iron, 8% nickel-18% chromium steel, 3.5% silicon-8% chromium steel, and mild steel.

## 3. VARIATION IN PROPERTIES OF THE MECHANICAL-TEST SPECIMENS

The mechanical-test specimens were tested after the runs at 300° and 500° C., and the average results compared with those from similar tests on specimens as received from the bright-annealing treatment. The mechanical properties tested were maximum stress, yield stress, percentage elongation, and hardness, for all the materials except tungsten wire, for which only maximum stress and percentage elongation were obtained.

No definite trend in these properties was observed with any of these materials after the tests at 300° C.

Some variations in the mechanical properties were observed after the tests at 500° C., and these were compared with control tests on specimens held at 500° C. under high-vacuum conditions for the same time intervals. This showed that the only variations which could definitely be ascribed to the influence of the mercury at 500° C. were decreases of approximately 50% in the maximum stress, yield stress, and elongation of commercial nickel. In addition, the percentage elongation of the tungsten wire appeared to have decreased about 50%, although more evidence would be needed to establish this definitely, for the wire was so brittle, even in the annealed state, that the elongation was small and difficult to measure.



## IV.—DISCUSSION

## 1. SOLUBILITY, WEIGHT LOSS, AND ATTACK

These investigations made it clear that in considering the attack of mercury on metals it is necessary to distinguish between the total weight lost and the solubility. For this reason the room-temperature results were obtained in terms of both the weight percentage loss and the weight percentage solubility. The weight loss is a better criterion of the total attack and is of practical importance, while the solubility is of more interest fundamentally.

The attack was frequently a complex process involving wetting of the surface, solution up to the saturation point consistent with the temperature, intergranular penetration by which whole crystals or larger aggregates were broken off, and the formation of intermetallic compounds which could also break off into the mercury. Thus, the mercury could contain the original metal and perhaps intermetallic compounds in solution, as well as undissolved particles of both and of their oxides.

The weight percentage solubilities would be in error if very small undissolved particles, perhaps even colloidal suspensions, passed the filter. The presence of such particles in the filtrate could not be observed visually owing to the opacity of the mercury, and would remain undetected by the techniques used. In fact, the solubilities determined at room temperature after the runs at 500° C. were frequently slightly higher than those from the corresponding runs at room temperature, perhaps owing to precipitation of very small or colloidal particles during the drop to room temperature. This effect could also be due to runs at room temperature, even of one or two thousand hours' duration, being inadequate for saturation, but this is unlikely.

Further, there were discrepancies between some determinations of the weight percentage loss for the same metal, not only as determined by weight losses, but also by chemical analysis. These were mainly due to amalgam formations which either remained intact on the specimens, or were partly broken off within the mercury, or wholly or partly broken or baked off after withdrawal from the mercury.

The attack on nickel illustrates these complexities. No attack was observed at room temperature, partial wetting occurred at 300° C., and complete wetting accompanied by severe intergranular attack and the formation of surface amalgams at 500° C. The severe penetration at 500° C. is illustrated by Fig. 3 (Plate V), which shows the effect of mercury attack followed by baking under vacuum, which evaporated residual mercury and the amalgam. The variable rates of attack for nickel at 500° C. given in Table I indicate the possibility of a "critical temperature" for attack at about 500° C.: tests at 450° and 550° C. supported this possibility. It is of interest to compare the remarks by Bailey and Watkins<sup>3</sup> on a critical temperature for the rate of spreading of mercury on copper.

The formation of intermetallic compounds of nickel and mercury at 500° C. was verified by X-ray analysis of freshly wetted surfaces by the surface-reflection technique. This showed the diffuse haloes of mercury, the characteristic patterns for nickel, and those of the

intermetallic compound NiHg<sub>3</sub>. In addition, an unidentified constituent, probably another mercury-nickel compound, was detected, although this could not be confirmed directly owing to the lack of X-ray data.

There was no significant intergranular attack or loss of mechanical strength with any of the mechanical-test specimens except nickel at 500° C. Despite this, the rates of attack of commercial nickel, Inconel, and Nimonic 75 were roughly comparable in the 500, 1000, and 2000-hr. tests, as shown in Table I. This emphasizes the fact that the weight-loss test does not give a full indication of the damage done, since serious intergranular penetration can occur without the grains dislodging, and thus without noticeable weight loss occurring. Such attack would be revealed only by microscopic examination or mechanical tests.

The tungsten wire samples appeared to suffer a form of attack at 500° C. which had no visible or microscopic effects, gave rise to no weight loss, and yet increased the brittleness. It is possible that minute surface cracks acting as "stress-raisers" were developed. The effect of surface imperfections in increasing the brittleness of notch-sensitive tungsten is well known.

## 2. PERIODIC-TABLE AND GRAPHICAL PRESENTATION

The periodic table of Fig. 1 shows the metallic elements divided into two main groups, the true metals and the B sub-groups. Most of the true metals crystallize in one of the three simple lattice structures, face-centred cubic, body-centred cubic, and close-packed hexagonal, whereas the B sub-group elements are structurally more complex and demonstrate a continuous transition from the metallic to the homopolar bond.

The group numbers I-VI inclusive, correspond to the highest valency of the metallic elements in that group, as shown for example by their highest oxides. The numbers 2-7 at the left-hand side give the number of the period, that is, the principal quantum number of the outer shell of electrons in the ground state.

Since the phases in alloy systems, such as primary solid solutions and intermetallic compounds, both of which occur in mercury amalgams, involve combinations which do not necessarily correspond with those expected from chemical principles of valency, it would not seem fruitful to attempt to relate the solubilities with chemical valency.

However, if these results are represented graphically, as in Fig. 2, which shows the atomic percentage solubility plotted against the atomic number, it is clear that the solubility at room temperature is a periodic function of the atomic number. The elements of each period are linked together so as to distinguish between the true metals and the sub-groups. The true metals are connected by firm lines, the B sub-group metals by dotted lines, and the two groups linked by chain lines. The pattern is repeated over the Long Periods 4, 5, and 6, with the maximum solubility for each period increasing with the period. To facilitate this diagrammatic representation, the solubility of mercury in mercury is taken to be infinitely high, and thus the chain line connecting gold to mercury, and the dotted line connecting mercury to thallium, are perpendicular.

Although the weight percentage losses at room temperature and at 500° C. show similar trends, the patterns

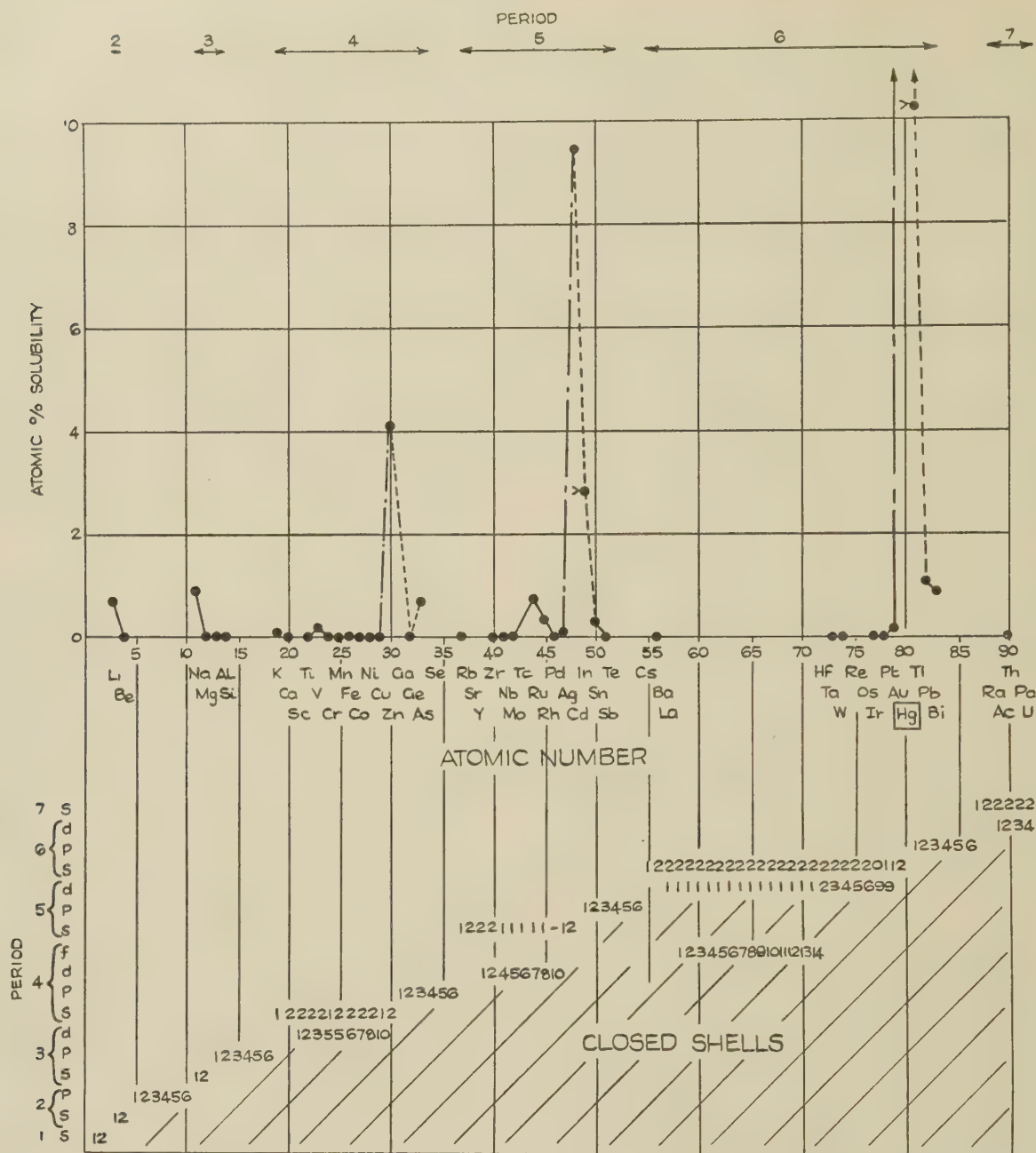


FIG. 2.—Solubility (Atomic Per Cent.) of Metallic Elements in Liquid Mercury at Room Temperature.

are not so well defined, as would be expected. Moreover, the matter is complicated at 500° C. by the low melting points of some of the metallic elements. It is significant that the low-melting-point elements exhibit the greatest room-temperature solubilities, for example the elements at the peaks of periods 4, 5, and 6. The transition metals suffered relatively insignificant attack, with the possible exceptions of manganese, nickel, zirconium, ruthenium, rhodium, palladium, platinum, and thorium, particularly at 500° C.

The possible relationship of solubility with the more detailed electronic structure is represented diagrammatic-

ally in Fig. 2 by splitting each shell into its *s*, *p*, *d*, and *f* sub-shells, corresponding to the azimuthal quantum numbers 0, 1, 2, and 3. The numbers 1, 2, &c., along the base of the figure give the number of electrons in each sub-shell for each metallic element: this detailed structure is taken from tables given by Born.<sup>4</sup> Consider, for example, nickel (atomic number 28). It is in the fourth period and has sub-shells 1*s*, 2*s*, 2*p*, 3*s*, and 3*p* completely filled: 3*d* is incomplete, with 8 electrons, while 4*s* is filled, with 2 electrons. This scheme for the distribution of electrons refers to free atoms in their normal states, not to atoms in a liquid or solid, and so



represents only an approximation to the finer structure in the liquid or solid states. Thus, although the electronic arrangement of the free nickel atom is  $(3d)^8(4s)^2$ , in the solid phase <sup>5</sup> it is said to average  $(3d)^{9.4}(4s)^{0.6}$ .

The suggested relationships brought out by these representations in Figs. 1 and 2 may be summarized as follows:

(1) Very low solubilities occur with the metallic elements whose outer *d* sub-shells are unfilled: scandium to nickel, yttrium to rhodium, lanthanum to iridium, and actinium to uranium: that is, roughly, the transition metals. Ruthenium and rhodium appear to be exceptions.

(2) The peak solubilities of the long periods 4, 5, and 6 occur where both the outermost *s* and *d* sub-shells are filled: zinc, cadmium, and mercury.

(3) The second highest solubilities of the long periods 4, 5, and 6 occur at the start of the outer *p* sub-shells: gallium, indium, and thallium. The solubility of gallium was not determined, but a search of recent literature <sup>6</sup> gives the value 3.6 at.-% at 35° C., which is in fair agreement with the value 1.8 at.-% at room temperature predicted from Fig. 2.

(4) The solubilities of the B sub-group elements are, in general, considerably higher than those of the true metals.

### 3. WETTING AND SURFACE OXIDE FILMS

The conditions of bright-annealing and storing of the specimens before test rendered them relatively free from surface films such as oxides, adsorbed gas, and water-vapour layers. However, since even residual surface films might conceivably protect the underlying metal against wetting and attack by the mercury, attempts were made with nickel, molybdenum, Inconel, and mild steel, to obtain completely film-free surfaces immediately before contact with the mercury. The most successful method tried was ion bombardment under high-vacuum conditions, followed by deposition of mercury on these freshly cleaned surfaces, in the same vacuum vessel.

The general conclusion from these tests was that, of the materials tested, those which wetted at room temperature under film-free conditions in the vacuum still also wetted in the bright-annealed state at 500° C. For example, nickel and Inconel wetted at room temperature, but only after ion bombardment, whereas both wetted at 500° C. in the bright-annealed condition. Thus, complete removal of the surface films from the specimens before the 500° C., and probably also the 300° C. tests, would not apparently have influenced the final results. The removal of surface films appears to expedite wetting without necessarily leading to further attack. In other words, wetting is an indication of incipient attack, but the magnitude of the final attack depends mainly on the temperature. This is not valid under dynamic conditions, where severe "erosion" may occur without any evidence of wetting.

Most of the metallic elements were baked under high vacuum at temperatures up to 500° C. immediately before the mercury was introduced. Thus, adsorbed gas and water-vapour layers would have been removed, although oxide layers would still have been present. The extent to which oxide layers alone could inhibit wetting and solution in the mercury therefore needs consideration, for this influences the time required for saturation.

The oxide film is removed in mercury either mechanically or by chemical reduction. The efficiency of the former depends on the strength and texture of the film and its adhesion to the base metal, while the latter depends on the relative free energies of formation of the metallic oxides and the oxides of mercury.

Table III gives the free energies of formation calculated from data found in the literature <sup>7</sup> for the oxides

TABLE III.—*The Free Energies of Formation of Crystalline Oxides of the Metallic Elements Based on Reactions Involving 1 Mole of Oxygen at Atmospheric Pressure.*

Metallic Oxide	Free Energies of Formation, kg.cal.	
	At 25° C.	At 500° C.
Au <sub>2</sub> O <sub>3</sub> . . . . .	+ 26	+ 47
Ag <sub>2</sub> O . . . . .	— 5	+ 10
PtO . . . . .	— 23	— 4
HgO . . . . .	— 28	— 3
PdO . . . . .	— 31	— 12
RhO . . . . .	— 36	— 18
CuO . . . . .	— 61	— 40
Tl <sub>2</sub> O . . . . .	— 65	— 35
The other metallic oxides from:		
Cu <sub>2</sub> O . . . . .	— 69	— 52
to		
CaO . . . . .	—289	—265

of the metallic elements studied in this investigation. The oxides are arranged in order of increasing free energies of formation and thus of increasing stability. Thus, mercury tends to reduce those metallic oxides above it in the Table, but not those below it. The order in the Table gives no indication of the reaction rates, so that even in the former case the time for reduction is unknown. Moreover, mercury does not oxidize readily in air at room temperature, although it does so more readily at 500° C. Thus, removal of the oxide layers by reduction appears unlikely, except perhaps with rhodium, palladium, silver, platinum, and gold at 500° C. For this reason the tests were continued for relatively long periods of up to 2661 hr., even with the five elements mentioned, since it was assumed that the protective oxide films could be broken down ultimately by mercury attack only at defects in the film. Further, as all the runs were conducted in the absence of air, film repair would be prevented. However, the results showed that a considerable degree of solution had occurred at room temperature after 6, 3, and 0.3 hr. for copper, silver, and gold, respectively, and probably also takes place fairly rapidly in several other cases. Again, palladium, silver, and gold wetted readily at room temperature, while platinum and rhodium wetted at 500° C. However, many of the metallic elements whose oxides are more stable than the mercury oxides also wetted readily, for example, lithium, manganese, copper, rubidium, cadmium, tin, lead, bismuth, and thorium at room temperature, the implication being that these oxide layers are defective or weak mechanically.

### 4. OXIDE SCUM ON MERCURY

A dark powdery scum of oxidized metal particles and solute frequently formed, sometimes rapidly, on the mercury surface when the specimen tubes were opened

to air at the end of the test run. Thus, dissolved metal was brought out of solution by this reaction and subsequently removed by the filtration process. If solution alone occurred, the metal content of the filtrate added to that of the residue would give the weight percentage solubility. However, since undissolved metal particles were often present as well, uncertainties in the chemical determinations of the solubilities arose. This difficulty could probably be avoided in future investigations by opening the tubes and filtering under an inert atmosphere.

The oxide scum was particularly noticeable with lithium, sodium, magnesium, aluminium, calcium, manganese, arsenic, zirconium, cadmium, tin, barium, thallium, and thorium, all of which are attacked by mercury, and whose oxides are more stable than those of mercury. It was not observed with silver, platinum, and gold, which are also attacked by mercury, and whose oxides are less stable than those of mercury. Thus the free energy of formation of the oxides seems to play a part in this phenomenon as well, although the reaction rates must influence behaviour considerably, for no serious oxidation was observed with copper, zinc, indium, antimony, lead, and bismuth, even though these metals also suffered considerable attack, and have oxides with free energies of formation exceeding those of the mercury oxides.

This oxidation phenomenon emphasized the importance of conducting the test runs in the absence of air. It probably also accounts for the relative ease with which mercury of an exceptionally high purity can be obtained. Moreover, it explains the well-known purifying action of bubbling dry air through mercury, subsequently removing the scum which forms.

It is reported in the literature <sup>8,9</sup> that the surface tension of mercury is anomalous and changes with time; according to Burdon and Oliphant <sup>9</sup> it decreases with time. It may be that this is due to gradual oxidation and removal from solution of traces of impurities initially dissolved in the mercury.

It is important to realize that the fact that oxidation of metals brings them out of solution in mercury means that, in the presence of air, continuous solution of these metals and deposition of their oxides could occur, giving rise to a form of mass transfer. This may be compared to the well-known type of mass transfer due to a thermal gradient, with metals whose solubility varies with the temperature.

##### 5. CAVITATION EROSION

Under dynamic conditions in mercury the attack can be greatly enhanced and altered in character. This was emphasized during investigations using ultrasonic vibrations, where the dynamic conditions gave rise to severe cavitation erosion at room temperature of the various materials tested, including aluminium, nickel, molybdenum, Inconel, and mild steel, but without wetting, the formation of amalgams, or solutions. None of these materials was attacked in static mercury at room temperature, and neither molybdenum nor mild steel suffered attack even at 500° C.

The effect of placing the probe of a 30-W. magnetostriction ultrasonic generator vibrating at 30 kc./s. on the surface of a nickel specimen while under mercury at room temperature is illustrated in Fig. 4 (Plate V). Microscopic examination showed that crystal fractures were transcrystalline; there was no evidence of intercrystalline attack. The specimen suffered severe erosion quite distinct from the type of attack under static conditions. Similar tests on Inconel proved that grains in the neighbourhood of cavitation pits were severely strained, implying that high pressures of several tons/in.<sup>2</sup> had developed. This supports, qualitatively, the theoretical predictions of high pressures developed by collapsing cavitation bubbles.<sup>10</sup>

In a discussion <sup>11</sup> on the nature of cavitation erosion, particularly with respect to ships' propellers, it was suggested that H<sup>+</sup> and OH<sup>-</sup> ions were an essential feature in the effect. The present experiments show, however, that cavitation can occur in the absence of these ions.

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# THE EFFECT OF HIGH AND LOW TEMPERATURES 1716 ON THE NOTCHED-BAR CHARACTERISTICS OF A CAST, HIGH-TENSILE, BETA-BRASS\*

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## SYNOPSIS

A  $\beta$ -brass of commercial manufacture, containing Cu 61.24, Zn 29.93, Al 5.04, Fe 1.34, Mn 2.07, Ni 0.15%, and with a tensile strength of 49 tons/in.<sup>2</sup>, has been examined in the notched-bar impact test over a range of temperatures. At room temperature, the Charpy figure was 28.5 ft.-lb., decreasing to 11 ft.-lb. at  $-195^{\circ}\text{C}$ .; fractures were transcrystalline in this range, although there was a small but significant tendency to intercrystalline cracking at room temperature, which gradually disappeared as the temperature of testing was lowered. The tendency to intercrystalline cracking was emphasized somewhat at  $100^{\circ}\text{C}$ ., and between  $200^{\circ}$  and  $650^{\circ}\text{C}$ . a brittle range, with intercrystalline fractures, was revealed, the alloy becoming plastic at more elevated temperatures.

Water-quenching after heating at  $500^{\circ}\text{C}$ . was apt to raise the impact-resistance at room and sub-zero temperatures; whereas quenching from higher temperatures, e.g.  $750^{\circ}\text{C}$ ., distinctly increased the intercrystalline weakness at room temperature and  $100^{\circ}\text{C}$ ., and this was also apparent at  $-195^{\circ}\text{C}$ .

The microstructure consisted of  $\beta$  grains, with the iron-bearing constituent dispersed within the grains and apparently in smaller form at the boundaries. The effect of heating above  $550^{\circ}\text{C}$ . was gradually to dissolve this constituent. There was no evidence that the intergranular constituent was the cause of the intercrystalline weakness.

## I.—INTRODUCTION

UNDER conditions of sustained tensile stress, either internal or of external application, high-tensile  $\beta$ -brasses are prone to intercrystalline cracking in air or, more especially, if in contact with sea-water or sodium chloride solution.<sup>1-6</sup> In the ordinary tensile test, the material possesses high strength accompanied by good elongation, the ultimate fracture being predominantly transcrystalline. However, tensile or bend tests with the specimen in contact with sea-water readily demonstrate the presence of the intercrystalline weakness, when it exists in a marked form.<sup>4,6</sup>

As part of a general programme of research on the mechanical characteristics of these alloys, and to determine whether the intercrystalline weakness could be revealed in other ways, a cast, 48-ton  $\beta$  alloy was tested in the Charpy notched-bar impact test over a range of temperatures from  $-195^{\circ}$  to  $800^{\circ}\text{C}$ . This alloy represents a type which has been shown to be particularly susceptible to the intercrystalline weakness.<sup>4,6</sup>

## II.—DETAILS OF ALLOY

The brass was of commercial manufacture to British Standard No. 1400-HTB3-C-1948, and contained Cu 61.24, Zn 29.93, Al 5.04, Fe 1.34, Mn 2.07, Ni 0.15%. It was sand cast into wedge test-bars (No. 1) according to British Standard No. 1367-1947, that is, with a large feeder running along the full length of the bar.

The microstructure of the alloy was typical (Figs. 2-4, Plate VI), consisting of fairly regular grains of the  $\beta$  phase (average grain dia. approximately  $\frac{1}{2}$  mm.), with well-dispersed particles of the iron-bearing constituent.<sup>4,6</sup> The tensile strength of 0.564-in.-dia. specimens was 49 tons/in.<sup>2</sup>, with an elongation of 20% on a 2-in. gauge-length. Susceptibility to intercrystalline weakness was confirmed by means of a bend test with the specimens in contact with sea-water.<sup>4</sup>

## III.—TESTING PROCEDURE

Charpy impact test-pieces with an Izod V-notch were used in a 15-kg. machine. For the sub-zero tests at temperatures down to  $-78^{\circ}\text{C}$ ., the specimens were cooled by immersion for 30 min. in a bath of methanol, the temperature of which was controlled by the addition of solid carbon dioxide. Initially, for the tests at  $-146^{\circ}\text{C}$ ., a bath of petroleum ether ( $40^{\circ}$ – $60^{\circ}\text{C}$ . boiling range) was used. This was contained in a copper beaker and was cooled by the evaporation of liquid nitrogen which was pumped around the beaker. However, it was found that at  $-146^{\circ}\text{C}$ . the bath was just beginning to thicken, and subsequent tests at  $-146^{\circ}$  and  $-150^{\circ}\text{C}$ ., using a bath of isopentane ( $27^{\circ}$ – $31^{\circ}\text{C}$ . boiling range) which remained liquid, gave slightly lower test figures which fitted better into the general run of results. The results for  $-160^{\circ}\text{C}$ . were obtained with a bath containing 1 part of petroleum ether to 10 parts of isopentane; and the tests at  $-195^{\circ}\text{C}$ . were made after the specimens had

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been immersed for 30 min. in liquid nitrogen. The temperature of the cooling bath was generally measured by means of a copper/Constantan thermocouple, although in a few of the later tests a thermometer, showing close agreement with the couple, was used. In all cases, the specimens were removed from the cooling medium, transferred to the machine, and tested within 6 sec.

For testing above room temperature, the specimens were heated in air for 1 hr. at the desired temperature in a small, hand-controlled electric furnace which was arranged beside the testing machine. At the end of this time, the specimens were transferred rapidly to the machine and tested. The temperature in each case was measured by means of a precious-metal thermocouple, the hot junction of which was inserted in a small hole drilled in one end of the specimen.

#### IV.—RESULTS OF CHARPY TESTS

The results of the tests are recorded in detail in Table I, and the general sequence is shown graphically in Fig. 1.

TABLE I.—Results of Charpy Notched-Bar Tests on As-Cast Alloy over Range of Temperatures.

Temperature, °C.	Energy Absorbed, ft.-lb.	Appearance of Fractured Surface
195	11	TRANSCRYSTALLINE, flat features, fawn in colour.
—160	17.5 †	"
—150	19 *	"
—146	22	"
—146 ¶	20 †	"
—78	24.5	TRANSCRYSTALLINE, but more finely torn texture.
—40	27	"
20	28.5	TRANSCRYSTALLINE, but finely torn texture throughout, except for a few intercrystalline faces.
100	23 ‡	TRANSCRYSTALLINE, but tendency for more intercrystalline faces.
200	8	INTERCRYSTALLINE, lustrous lemon-yellow appearance.
300	5 ‡	"
400	1	INTERCRYSTALLINE, but " slightly more golden in appearance.
500	1	INTERCRYSTALLINE, but distinctly golden in appearance.
600	1.5 ‡ §	"
650	4 *	INTERCRYSTALLINE, but " end of fracture just incomplete.
700	21 *	Partly broken exposing lustrous, golden-coloured crystal faces. Unbroken region showed plastic flow.
750	27 *	Not broken, considerable plastic flow, some porosity exposed.
800	40 *	Not broken, considerable plastic flow. Beginning to tear near notch, showing preference for intercrystalline path.

Unless otherwise stated the figures given are the averages of three, generally close, results. \* One determination. † Two determinations. ‡ Four determinations. § One specimen tested after 3 hr. at temperature. || Cooling bath of petroleum ether. ¶ Cooling bath of isopentane.

The tests at sub-zero temperatures exhibited a steady decrease in impact-resistance from room temperature down to  $-150^{\circ}\text{C}.$ , but from the latter temperature

down to  $-195^{\circ}\text{C}.$  the decrease in resistance was considerably more rapid. Nevertheless, the actual test figure for  $-195^{\circ}\text{C}.$  was not insignificant. The fractured surfaces of the specimens tested at sub-zero temperatures presented an almost completely transcrystalline appearance. Fracture at room temperature was also predominantly transcrystalline, although a few intercrystalline facets were apparent, and odd facets of this nature were probably not completely absent from the sub-zero specimens. The fractures at room temperature had a fine although rough or torn texture, but as the temperature of testing was lowered the roughened appearance

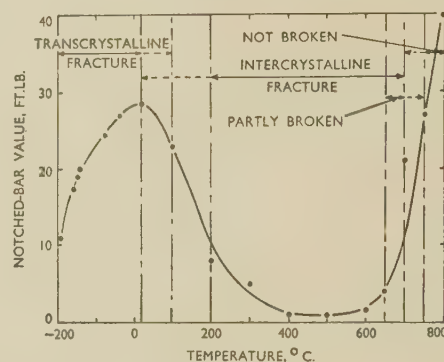


FIG. 1.—Results of Charpy Tests on As-Cast Alloy. The extent of intercrystalline cracking at room temperature is small but nevertheless significant.

gave way to flatter features of somewhat more crystalline form.

At  $100^{\circ}\text{C}.$  some of the fractures showed an increased number of intercrystalline faces and definite weakening was experienced. A brittle range occurred from  $200^{\circ}$  to  $650^{\circ}\text{C}.$ , the fractures being intercrystalline and presenting a bright and lustrous appearance. There was increased resistance above  $650^{\circ}\text{C}.$ , the specimens undergoing plastic flow and not breaking completely in the test. At  $750^{\circ}$  and  $800^{\circ}\text{C}.$ , the specimens were essentially unbroken.

During some preliminary experiments at high temperatures specimens were tested after heating in a furnace situated at some distance from the testing machine. This involved transfer of the specimens from the furnace at temperatures considerably higher than those of ultimate testing. The specimens thus underwent air-cooling for approximately  $\frac{1}{2}$  min. during transfer. Later, when a furnace was installed beside the testing machine and when the procedure described earlier was adopted, it was found that there was a marked difference in the results for the higher-temperature tests. Those specimens tested after air-cooling from higher temperatures offered considerably greater impact-resistance than those heated directly to the testing temperature, although if an air-cooled specimen was held at the test temperature for 1 hr. the higher resistance was not obtained. Several experiments were carried out especially to illustrate the magnitude of this effect; the results are given in Table II.

Specimens were also tested after heating in air at temperatures covering the brittle and plastic ranges, i.e. at  $50^{\circ}$  or  $100^{\circ}$  intervals from  $400^{\circ}$  to  $800^{\circ}\text{C}.$ , followed by air-cooling or water-quenching. Air-cooling from eight selected temperatures raised the resistance to fracture at



room temperature by on an average 2 ft.-lb., without materially affecting the nature of the fracture. The tests on the water-quenched specimens revealed two interesting points.

First, although water-quenching from 400° C. had no significant effect, quenching from 500° C. caused a greater degree of toughening (than did air-cooling) at room temperature. Further tests showed that the improvement was maintained at sub-zero temperatures, but not at 200° C. (Table III). In each test on material quenched

—195° C., and was more prevalent than in the as-cast condition at 100° C. A 0.282-in.-dia. specimen, water-quenched after 1 hr. at 750° C., had, at room temperature, a tensile strength of 42 tons/in.<sup>2</sup> and an elongation of 10% (on 1 in.). The fracture showed a distinct intercrystalline tendency.

TABLE IV.—Results of Charpy Tests at Various Temperatures on Specimens Water-Quenched from 750° C.

Corresponding results for the cast condition are given in parentheses.

Time of Heating, hr.	Temperature of Testing, °C.	Energy Absorbed, ft.-lb.*
1	–195	12 (11)
1	Room temperature	27 (28.5)
9	”	27.5 (28.5)
9	100	21 (23)

\* Single result.

Generally, the tests on the heat-treated specimens were carried out directly after treatment; in the case of specimens water-quenched from 500° C., however, the behaviour on testing directly at room temperature was compared with that after three days had elapsed; no significant difference in Charpy figures was found.

## V.—METALLOGRAPHIC EXAMINATION

The specimens for metallographic examination were prepared by a technique described elsewhere,<sup>7</sup> which uses diamond abrasives for rough polishing; finish polishing of these particular specimens was carried out by skidding on a magnesium oxide paste containing a small concentration of ammonium persulphate. The specimens were etched in a warm 10% ammonium persulphate solution.

### 1. GENERAL MICROSTRUCTURE

The cast alloy was relatively coarse-grained, with grain boundaries of the usual smooth contours. Large particles of the iron-bearing constituent, grey-blue in colour and often of star-like shape, occurred in the structure, being located mostly within the grains; in addition much finer star-shaped particles were present (Fig. 2, Plate VI). Fine rounded particles, presumably of the same constituent, were also present in the grains; particles of similar shape, but tending to be larger, were frequently distributed also along the grain boundaries (Figs. 2 and 3, Plate VI), as well as distinctly larger and more elongated pieces (Fig. 4, Plate VI). Electrolytic polishing and etching did not develop any evidence of pitting or grooving at the grain boundaries, other than that which could be accounted for by the presence of the iron-bearing constituents.

Specimens were examined after treatment for 1 hr. at 400°, 500°, and thereafter usually at 50° intervals up to 850° C. Heat-treatment at 400°–550° C. had no significant effect on the microstructure. However, at higher temperatures the following progressive changes were noted: (a) Starting at 600° C., the grain-boundary constituents and the finer constituents inside the grains dissolved, this process being complete at 725° C.; and (b) from 725° C. upwards the larger particles of the iron-

TABLE II.—Effect of Previous Heating on Notched-Bar Characteristics at Elevated Temperatures.

	Conditions of Heating	Energy Absorbed, ft.-lb.	Fracture
1	Heated at 600° C. for 1 hr.	1.5 *	INTERCRYSTALLINE, lustrous golden appearance.
2	Heated at 725° C. for 1 hr. and air-cooled to 600° C.	13 †	As (1), but not quite completely broken. Unbroken region showed plastic flow.
3	Heated at 725° C. for 1 hr., air-cooled to 600° C., and maintained at that temperature for 1 hr.	1 †	As (1).
4	Heated at 650° C. for 1 hr.	4 †	As (1), end of fracture just incomplete.
5	Heated at 750° C. for 1 hr. and air-cooled to 650° C.	14 †	As (2).

\* Based on three results.

† Single result.

TABLE III.—Results of Charpy Tests at Various Temperatures on Specimens Water-Quenched after Heating for 1 hr. at 500° C.

Corresponding results for the cast condition are given in parentheses.

Temperature of Testing, °C.	Energy Absorbed, ft.-lb.
–195	18 † (11)
–78	29 † (24.5)
Room temperature	34 * (28.5)
200	8 † (8)

\* Based on three results.

† Single result.

from 500° C., the fracture was comparable with that of as-cast material at the corresponding temperature. The tensile characteristics at room temperature of a 0.564-in.-dia. specimen after water-quenching from 500° C. (heated for 1 hr.) were: tensile strength 44 tons/in.<sup>2</sup>, elongation 10% (on 2 in.). The fracture, although preceded by less deformation, followed a similar path to that in the as-cast alloy.

The second point of significance was that quenching from higher temperatures caused a more pronounced tendency to intercrystalline fracture at room temperature without greatly affecting the resistance to fracture. In general, this tendency appeared to increase with increase in the temperature from which the quenching was carried out. The effect is well illustrated by the tests on specimens quenched from 750° C. (Table IV), in which it was found also that the intercrystalline cracking persisted at

bearing phase were noticeably reduced in size, and consequently became less angular. Water-quenching retained these conditions (Fig. 5, Plate VI). On the other hand, during air-cooling, precipitation of a large number of fine particles occurred both within the grains and at the boundaries (Fig. 6, Plate VI); some of these particles were large enough to be resolved as being of a star-like shape.

With regard to the results in Table II, specimens were heated at 725° C. for 1 hr. and then air-cooled to 600° C. One specimen was water-quenched directly, and another held at this temperature for 1 hr. before water-quenching. The structures were of the same type as that shown in Fig. 6.

Certain of the impact specimens, both in the cast and heat-treated conditions, exhibited deformation-band markings adjacent to the fracture surface (Fig. 7, Plate VII) similar to those for binary  $\beta$ -brass recently described in detail by Barrett.<sup>8</sup> In all cases, the existence of deformation in the grains was confirmed by rippling on the surface of the specimens, adjacent to the point of fracture. The markings were most prominent in specimens tested at room temperature; they were usually present in specimens tested at sub-zero temperatures, although to a decreasing extent, so that only very faint signs were visible in specimens broken at -195° C. The markings were also found in specimens broken at 100° C., and to a slight degree at 200° C., but not in specimens broken at higher temperatures. Barrett,<sup>8</sup> on the other hand, found prominent bands in material deformed at temperatures from -195° C. to at least 400° C., but this was in specimens deformed in an entirely different manner, namely, by slow or impact compression.

The overall impression was that the degree of development of the deformation-band markings was approximately related to the impact-resistance of the specimens tested at room and sub-zero temperatures. This indicates that the variation in the impact values of these specimens is dependent upon the mechanism of deformation of the individual grains, a factor which is outside the scope of the present investigation. It is, however, relevant to mention that Barrett<sup>8</sup> found that there was a moderate increase in impact hardness as the temperature was lowered from 20° to -195° C. Further, it should be noted that the present results could be explained by the suggestion of Kramer and Maddin<sup>9</sup> that flow-temperature brittleness in body-centred cubic metals is due to delay in the initiation of slip, their supporting evidence being for single crystals of binary  $\beta$ -brass, as opposed to  $\alpha$ -brass and aluminium, in which no delay was experienced.

## 2. NATURE OF FRACTURED SURFACES

In general, the metallographic examination served only to confirm the information derived from the external appearance of the fractured surfaces. The fractures of the cast specimens tested in the range -195° to 100° C. were predominantly transcrystalline (Fig. 7, Plate VII) but as the impact temperature was raised in this range, a small number of intercrystalline faces appeared in the fracture. This was noticeable to any significant extent only at room temperature and 100° C., where, in addition, a few short intercrystalline cracks ran transversely from the fractured surface. Slight evidence of such cracking was found also in specimens tested at -40° and -80° C.

A similar tendency was noted with the tensile specimens of the as-cast alloy (tested at room temperature), and after water-quenching from 500° C., in which deformation markings were quite pronounced.

Charpy specimens tested in the range 200°-650° C. gave intercrystalline fractures, often with the associated intercrystalline cracks (Fig. 8, Plate VII). At 200° C. there were occasional and very short transcrystalline regions, with associated deformation bands; from 500° to 650° C. a small amount of recrystallization was revealed at a few places on the fractured surfaces. Elongated grains were present in the region of the notch in specimens tested at 700°-800° C., and the beginning of recrystallization was apparent. Where partial cracking or tearing had started, this was intercrystalline or showed preference for an intercrystalline path (Table I).

In the specimens broken or heat-treated at 400° C. and above, a layer of small recrystallized grains was often present at the machined surfaces. This layer must have resulted from the deformation caused in machining.

The fractures of the heat-treated specimens differed little from those of the as-cast material tested at the same temperature, except in the case of specimens water-quenched from above 500° C., which showed an increasing tendency to intercrystalline weakness. This was particularly prevalent after quenching from 750° C., when, for example, after testing at room temperature, about half the fracture was intercrystalline and severe transverse intercrystalline cracks were present (Figs. 9 and 10, Plate VII).

## VI.—CONCLUSIONS AND DISCUSSION

Charpy notched-bar testing shows that a slight tendency to intercrystalline cracking exists at room temperature in the complex  $\beta$  alloy, as-cast, and that this is somewhat increased when the temperature is raised to 100° C. At higher temperatures, a range of pronounced intercrystalline brittleness is revealed between 200° and 650° C., these figures being in approximate agreement with a brittle range of 226°-558° C. quoted by Smalley<sup>10</sup> for  $\beta$  copper-zinc-aluminium alloys, and 220°-540° C. found by Bunting<sup>11</sup> in a binary  $\beta$ -brass. Moreover, the fact that in the present work a fairly noticeable tendency to intercrystalline cracking was obtained at 100° C., means that the results show reasonable accord with recent figures due to Perryman,<sup>12</sup> who reported the existence of a range of intercrystalline weakness between 100° C. and 400° or 500° C., detected by means of an impact tensile test, in binary  $\beta$ -brass and ternary aluminium-bearing alloys.

If the intercrystalline weakness experienced in the alloy at room temperature (in the Charpy test and under sustained tensile stress) was due to some condition established at the crystal boundaries during cooling through the brittle range, it might be expected that a specimen, held for some time in the brittle range and quenched, would be subject to greater intercrystalline weakness at room temperature; and, alternatively, that quenching from higher temperatures in the plastic range would inhibit the weakness. It was with these points in mind, that the tests on the heat-treated specimens were carried out. However, the results showed that quenching after heating at 500° C. was apt to toughen the alloy at room and at sub-zero temperatures without creating



any extra tendency to intercrystalline cracking. On the other hand, water-quenching from higher temperatures and especially from the plastic range (e.g. from 750° C.) increased the tendency to intercrystalline cracking in the Charpy test at room temperature, as well as at 100° C., and even rendered it quite prevalent at -195° C.

These results were substantiated to a considerable extent by the results of a few trial bend tests on heat-treated material in air and in contact with sea-water. Specimens which had been water-quenched after heating at 500° C. for 1 hr. were indistinguishable in behaviour from those of the as-cast material, withstanding considerable deformation before undergoing transcrystalline fracture in air, and showing intercrystalline failure with less deformation when in contact with sea-water. Specimens quenched after 1 hr. at 750° C. appeared to be weaker in sea-water and to give a more lustrous intercrystalline fracture than did the as-cast alloy; they suffered less deformation in air, and the fracture revealed a definite tendency to follow an intercrystalline path.

There is no evidence to suggest that the grain-boundary constituent observed in the alloy is the cause of the intergranular weakness, since: (1) similar weakness occurs in other  $\beta$ -brasses which do not contain this constituent,<sup>6, 12, 13</sup> and (2) conditions which remove or tend to remove the constituent, i.e. quenching from high temperatures, increase the weakness. It is true that the restoration of plasticity at elevated temperatures does coincide approximately with the disappearance of the grain-boundary constituent. However, this is not considered to be significant, indicating only that the tendency to intercrystalline weakness has been overshadowed by the general increase in the plasticity of the material.

In his recent work, Perryman<sup>12</sup> has suggested that intercrystalline cracking of  $\beta$ -brasses may be due to the relaxation of shear stresses across certain grain bound-

aries, primarily by means of viscous flow, thus causing stress concentrations and cracking at other boundaries. Such cracking would be favoured by an increase in temperature or by a decrease in strain rate. This explanation might fit the cracking of the complex alloy at elevated temperatures in the Charpy test, although it is scarcely conceivable that viscous movement can occur under these conditions. Moreover, the concept is clearly unsuitable with respect to the intercrystalline cracking at room temperature of the alloy, especially after it has been water-quenched from a high temperature such as 750° C., in which case the weakness is maintained at sub-zero temperatures.

#### ACKNOWLEDGEMENTS

The authors wish to acknowledge facilities for using the Charpy testing equipment provided by Messrs. Head, Wrightson and Co., Ltd., Thornaby.

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# 1717 THE CONSTITUTION OF TIN-INDIUM ALLOYS IN THE RANGE 0-30 PER CENT. INDIUM\*

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## SYNOPSIS

Equilibrium relationships at the tin-rich end of the tin-indium diagram have been investigated. 8% of indium is soluble in tin at 205° C. and about 6% at 50° C. A second solid solution is formed by a peritectic reaction at 205° C. This phase extends from 14.2 to 24% indium at 50° C.

## I.—INTRODUCTION

THE results of a number of investigators of the tin-indium system are in substantial agreement over the composition range 30-100% indium, but data on the tin-rich alloys appear to be incomplete and contradictory. Available information suggests that indium is one of the relatively few metals which have appreciable solid solubility in tin, and it was considered that a more detailed study of the constitution of the tin-rich alloy would be of interest.

## II.—PREVIOUS WORK

The first systematic investigation of the system was undertaken by Fink, Jette, Katz, and Schnettler,<sup>1</sup> who gave the solubility of indium in tin as 1.5% and that of tin in indium as 10%. They also reported the formation of two intermediate phases, one ( $\gamma$ ) existing around 10% indium, and the other ( $\beta$ ) around 75% indium. Later work by the same authors<sup>2</sup> suggested that  $\gamma$  and  $\beta$  were formed as a result of peritectic reactions at 124.0° and 126.5° C., respectively, and showed that the two phases formed a eutectic melting at 116.3° C. and containing 52% indium. This confirmed the earlier work of Valentiner.<sup>3</sup>

Valentiner, however, demonstrated that the solid solubilities were much higher than indicated by Fink *et al.* in their earlier paper,<sup>1</sup> and reported values of 15% for tin in indium and 7% for indium in tin. He deduced from X-ray-diffraction patterns that the structures of both  $\gamma$  and  $\beta$  were tetragonal and gave them the formulae  $\text{InSn}_{15}$  and  $\text{In}_6\text{Sn}_2$ , respectively.

The system was re-investigated by Rhines, Urquhart, and Hoge<sup>4</sup> by classical methods. They confirmed in most respects the earlier work on the indium-rich alloys, but could not find the peritectic reaction at 124° C. reported by Fink *et al.*<sup>2</sup> Instead they proposed that  $\gamma$  was formed by a peritectoid reaction at some temperature below 80° C.

Recent work by Raynor and Lee<sup>5</sup> on the intermediate phases of some tin-rich alloys shows that  $\gamma$  is hexagonal and not tetragonal as suggested by Valentiner.<sup>3</sup> The

hexagonal structure has also been found by Screaton and Ferguson.<sup>6</sup>

The diagram of Rhines *et al.*,<sup>4</sup> which includes the results of their own work and that of previous investigations is reproduced in Fig. 1.

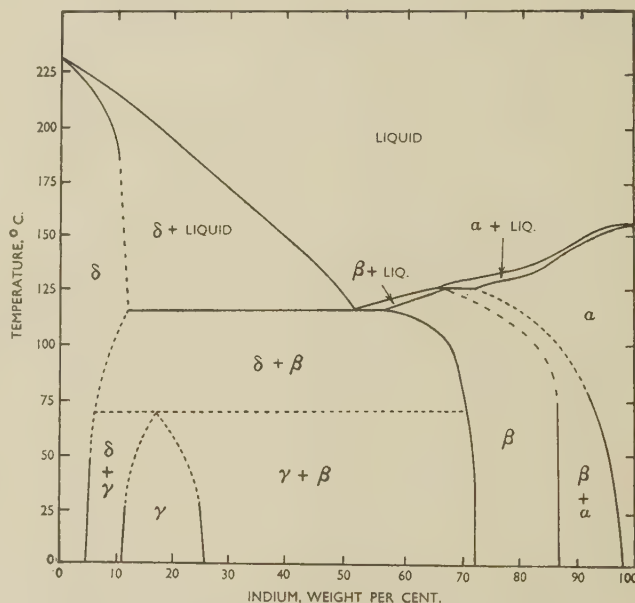


FIG. 1.—Equilibrium Diagram of the Tin-Indium System. (After Rhines *et al.*)

## III.—EXPERIMENTAL

The alloys were prepared from tin and indium of not less than 99.98 and 99.95% purity, respectively. Those used for metallographic and X-ray examination were melted in Salamander crucibles and chill cast to give ingots 1 × 0.25 in. in cross-section. Thermal analysis was carried out on samples made up and remelted in small silica crucibles. After thermal analysis the contents of the crucible were chill cast and samples for chemical analysis taken. Rates of heating and cooling

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§ All figures quoted are in weight per cent. Differences between weight and atomic per cent are not great. For example 10, 20, and 30 wt.-% indium are equal to 10.2, 20.4, and 30.6 at.-% indium, respectively.



were about 1° C./min. The values used for plotting the liquidus were the arithmetical means of the values obtained for heating and cooling. Generally, these temperatures did not differ by more than 0.5° C. Thermal analysis was used to determine the liquidus and the eutectic temperatures and to search for changes in the solid state. However, no indication of any change in the solid was found.

Alloys were brought to equilibrium by annealing before metallographic or X-ray examination. Thermal analysis indicated eutectic arrests in alloys containing as little as 9% indium and all chill-cast samples were therefore given a preliminary homogenizing treatment for 16 days at 110° C. For the determination of the phase boundaries in the solid state specimens previously homogenized at 110° C. were annealed, first at 200° C. and then successively at the lower temperatures (Table I). Where more than one annealing time was used, no change in the phase limits was found after the longer time. For the determination of the solidus, samples were annealed for 16 hr. at progressively higher temperatures (5° C. steps), quenched, and examined for signs of fusion. Above 175° C. the annealing time was reduced to 4 hr.

TABLE I.—Annealing Treatments for Samples Previously Homogenized for 16 days at 110° C.

Annealing Temperature, °C.	Annealing Time
200	100 hr.
192	" "
178	" "
150	200 "
126	14 days
100	10 and 20 days
75	14 days
50	7 and 14 days

The etching characteristics of the  $\delta$  and  $\gamma$  phases are similar, and it is very difficult to distinguish between them by metallographic means. Many etchants were tried, and the most generally useful proved to be a 2% solution of concentrated hydrochloric acid in alcohol. With this solution the  $\gamma$  phase is attacked slightly more rapidly than  $\delta$  in alloys containing a small quantity of  $\gamma$  in  $\delta$ . When the alloy contains small quantities of  $\delta$  in  $\gamma$ , however, the two cannot be distinguished. In view of the uncertainty associated with etching, the  $\delta/(\delta + \gamma)$  and  $(\delta + \gamma)/\gamma$  boundaries were determined by X-rays, using the disappearing-phase method. Normally, it would have been preferable to employ the changes in lattice constant with composition to determine the exact boundaries, but the changes observed were too small to allow the boundaries to be determined with sufficient accuracy. The disappearing-phase method leads to errors on account of the difficulty of detecting small quantities of a second phase by X-ray diffraction. The errors have the effect of extending the single-phase regions. Where it has been possible to check the  $\delta/(\delta + \gamma)$  boundary by metallographic means, it is estimated that the solubility of indium in tin given by the X-ray results is about 0.5% too high. The  $\gamma/(\gamma + \beta)$  boundary was found by microexamination of quenched specimens, the  $\beta$  phase being preferentially attacked by a 2% solution of concentrated hydrochloric acid in alcohol. In the determination of the solidus, etching

with the same reagent clearly revealed the presence of quenched liquid.

To confirm the existence of the peritectic horizontal at 205° C. small strips of alloy were heated in a furnace at the rate of 1° C./min. while under slight tension and the temperature noted at which failure occurred. The samples, containing from 7 to 10% indium, were rolled from homogenized ingots and brought to equilibrium by annealing for 10 days at 180° C. This technique has been shown by Homer and Plummer<sup>7</sup> to give a good indication of the solidus in tin-base alloys.

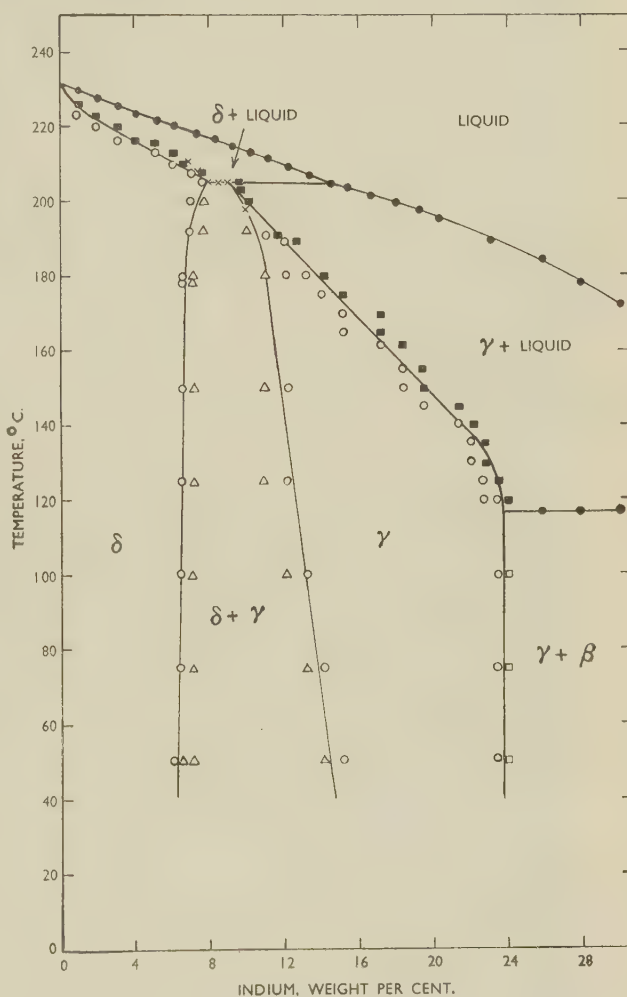


FIG. 2.—Equilibrium Diagram of the Tin-Indium System up to 30% Indium. (Present work.)

#### IV.—RESULTS AND DISCUSSION

The equilibrium diagram constructed from the results obtained is given in Fig. 2. This differs from previous diagrams in that the  $\gamma$  phase is shown to result from a peritectic reaction at 205° C. The evidence for this reaction is to some extent indirect, since no thermal arrest was observed in spite of many attempts to find one. The reasons for interpreting the experimental results as indicating a peritectic reaction are that there is a slight inflection in the liquidus curve and a marked inflection in the solidus at 205° C. and that the phases  $\delta$  (tetragonal)

and  $\gamma$  (hexagonal) are of different although related structures. The structural differences were evident from diffraction patterns of alloys quenched in the temperature range 50°-200° C. In addition, the fracture tests at elevated temperatures indicate a small horizontal in the solidus curve between 8 and 9% indium. An alternative interpretation would be that the  $\delta$  and  $\gamma$  phases were enclosed in a loop in a similar way to the  $\alpha$  and  $\alpha'$  phases in the aluminium-zinc system. This interpretation is, however, rejected because the  $\delta$  and  $\gamma$  phases have different structures, whereas the phases found in systems with closed loops are of the same structure but different lattice spacings.

The  $\delta/(\delta + \gamma)$  and  $(\delta + \gamma)/\gamma$  boundaries are plotted from the X-ray results. As already pointed out in the section on experimental work, this is likely to result in the first boundary being displaced towards the indium-rich end and the second towards the tin-rich end of the diagram. The error in such cases is likely to be less than  $\frac{1}{2}\%$ , and it was deemed preferable to accept this error rather than to employ values derived from metallographic examination, which are, in the opinion of the present authors, rather less reliable in this part of the diagram.

The mechanical properties of these alloys have not been investigated in the present work, but it is of interest that Jaffee and Weiss<sup>8</sup> found that the tensile strength/composition curve shows maxima at about 6

and 20% indium. These correspond fairly closely with the  $\delta/(\delta + \gamma)$  and  $\gamma/(\gamma + \beta)$  boundaries as determined by the present work. The trough between the maxima occurs at about 10% indium, corresponding with the centre of the  $(\delta + \gamma)$  phase field. Hardness and compressive strength follow tensile strength closely, but the figures for elongation show a maximum at 6 and a minimum at 20% indium.

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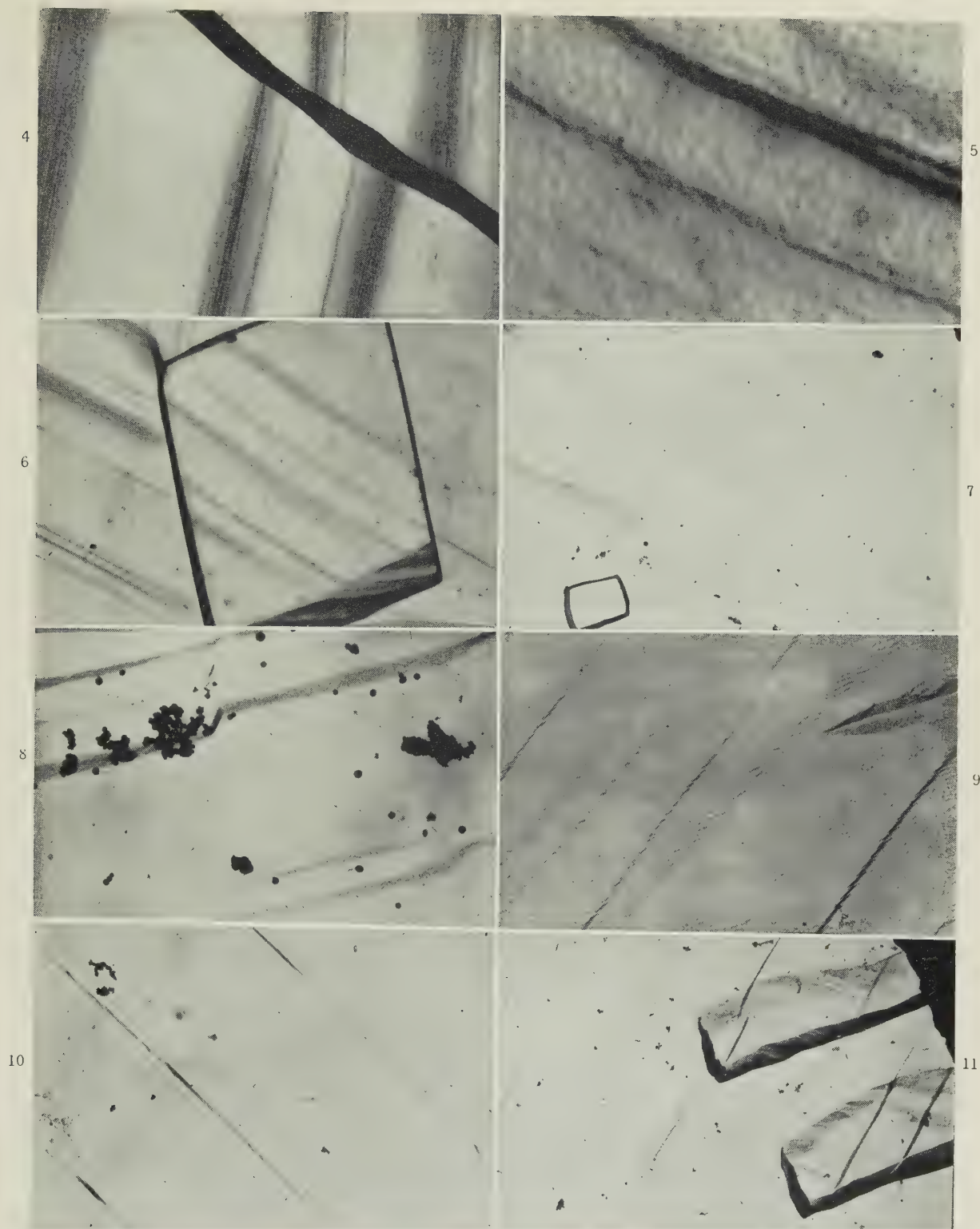


FIG. 4.—High-Purity Aluminium. Water-quenched after 21 hr. at 620° C.; etched in Lacombe's reagent; elongated 80%.  $\times 12,500$ .

FIG. 5.—Al-1% Mg. Water-quenched after 4 hr. at 425° C.; elongated 10%.  $\times 42,000$ .

FIG. 6.—As Fig. 5. Etched in Lacombe's reagent; elongated 20%.  $\times 10,500$ .

FIG. 7.—Al-3% Mg. Water-quenched after 4 hr. at 425° C.; etched in Lacombe's reagent; elongated 15%.  $\times 2100$ .

FIG. 8.—As Fig. 7. Elongated 25%. Showing double faulting.  $\times 12,750$ .

FIG. 9.—Al-5% Mg. Water-quenched after 4 hr. at 425° C.; etched in Lacombe's reagent; elongated 15%.  $\times 11,000$ .

FIG. 10.—Al-5% Mg. Water-quenched after 4 hr. at 425° C.; elongated 25%.  $\times 10,500$ .

FIG. 11.—Al-7% Mg. Water-quenched after 4 hr. at 425° C.; etched in Lacombe's reagent; elongated 20%.  $\times 3500$ .

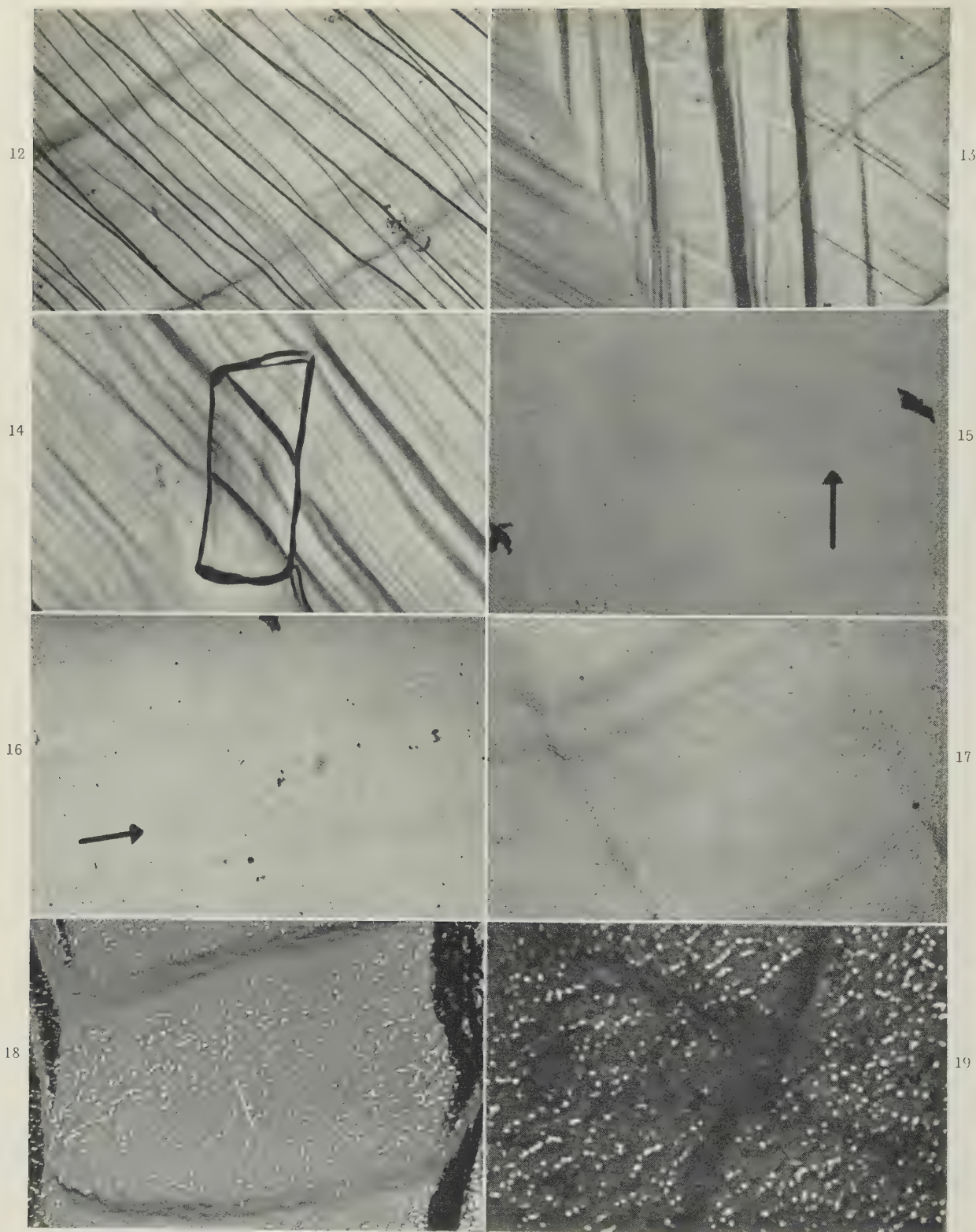


FIG. 12.—As Fig. 11. Elongated 35%.  $\times 3500$ .

FIG. 13.—As Fig. 12. Elongated 40%.  $\times 3500$ .

FIG. 14.—Al-7% Mg. Water-quenched after 4 hr. at 425° C.; etched in Lacombe's reagent; elongated 30% in liquid air.  $\times 5300$ .

FIG. 15.—Al-1% Ag. Water-quenched after 4 hr. at 420° C.; elongated 10%. Fine slip visible in direction of arrow.  $\times 10,500$ .

FIG. 16.—Al-5% Ag. Water-quenched after 4 hr. at 420° C.; elongated 5%. Fine slip visible in direction of arrow.  $\times 10,500$ .

FIG. 17.—As Fig. 16. Elongated 25%.  $\times 10,500$ .

FIG. 18.—Al-4% Cu. Water-quenched after 4 hr. at 535° C.; etched in Lacombe's reagent; elongated 30%. Note absence of white spots in the region of the slip bands.  $\times 21,000$ .

FIG. 19.—As Fig. 18. Showing distortion at region of duplex slip.  $\times 42,000$ .



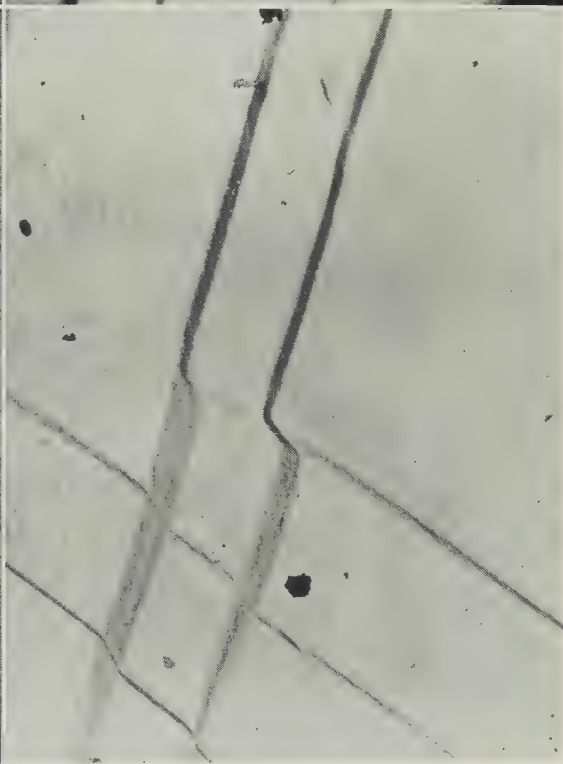
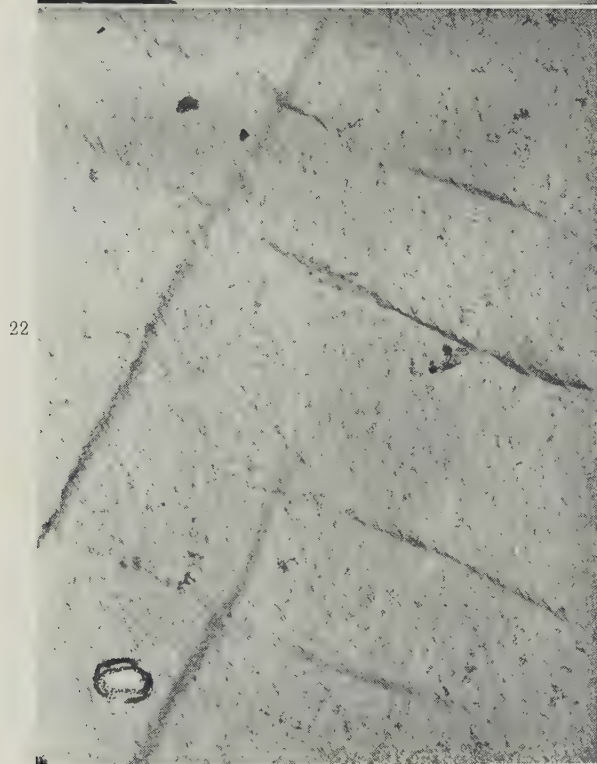
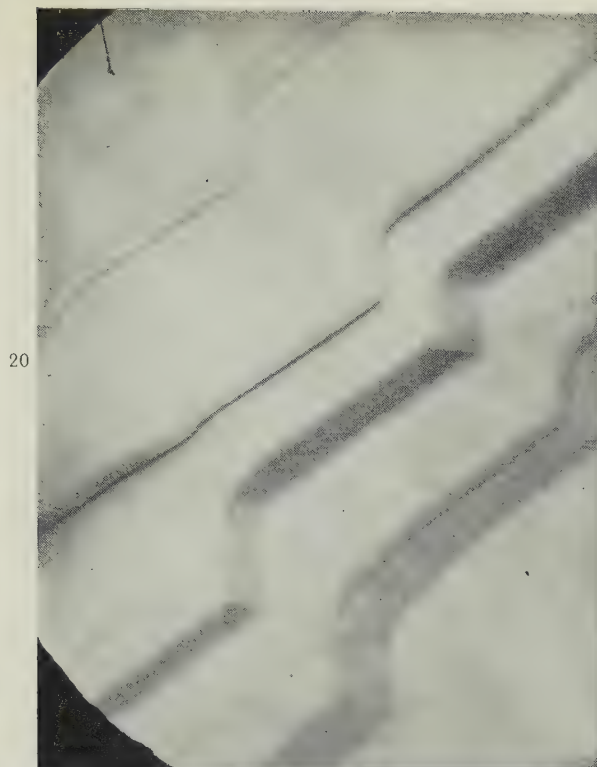
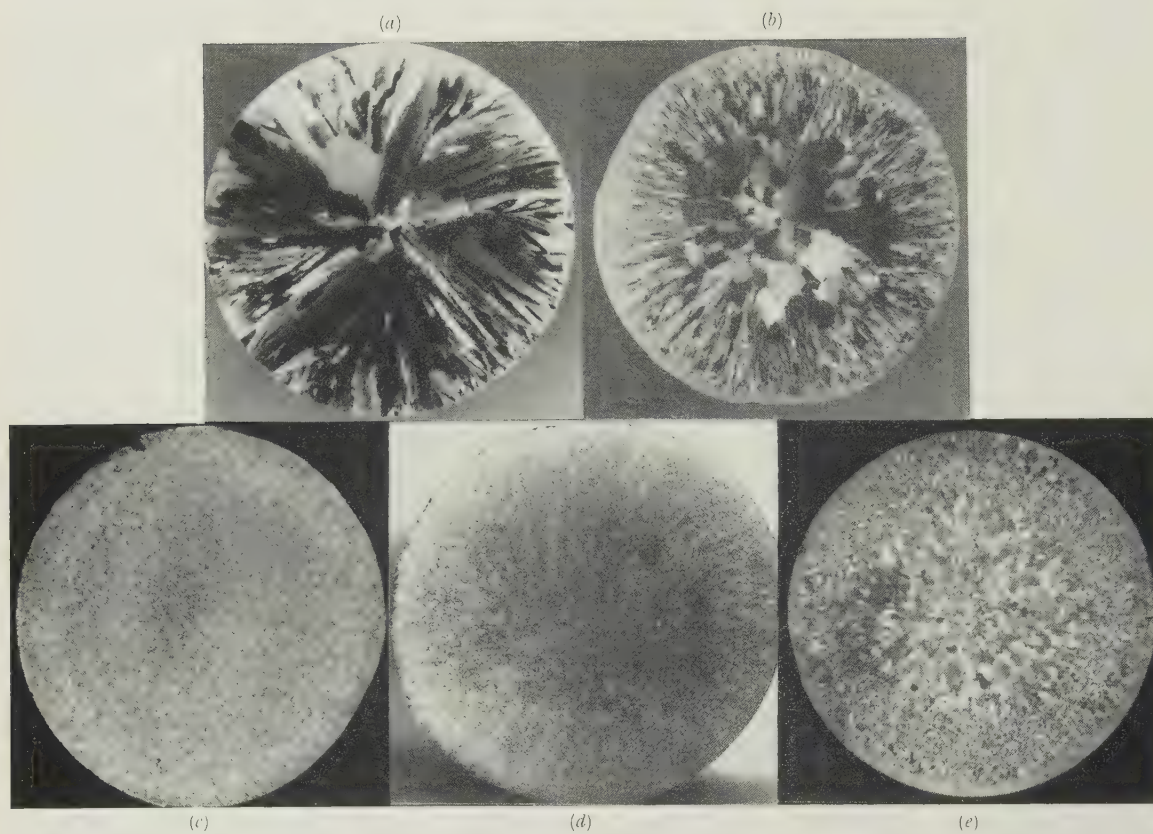


FIG. 20.—High-Purity Aluminium. Water-quenched after 3 hr. at  $600^{\circ}\text{C}.$ ; elongated 40%.  $\times 12,500$ .

FIG. 21.—As Fig. 20. Etched in Lacombe's reagent; elongated 12% in liquid air. Showing complex duplex slip.  $\times 12,500$ .

FIG. 22.—Al-4% Cu. Water-quenched after 4 hr. at  $535^{\circ}\text{C}.$ ; etched in Lacombe's reagent; elongated 30%.  $\times 10,500$ .

FIG. 23.—Al-3% Mg. Water-quenched after 4 hr. at  $425^{\circ}\text{C}.$ ; elongated 35%. Showing formation of lamellæ as a result of duplex slip.  $\times 12,750$ .



FIGS. 1 (a)-(d).—Transverse Sections of Laboratory Ingots of Copper-Aluminium Alloys.  $\times \frac{3}{8}$ .

(a) 7.5% Al, (b) 7.5% Al with 0.10% V, (c) 8.38% Al with 0.02% B, (d) 8.34% Al.

FIG. 1 (e).—Commercial Ingot 8.37% Al with 0.02% B.  $\times$  approx.  $\frac{1}{8}$ .



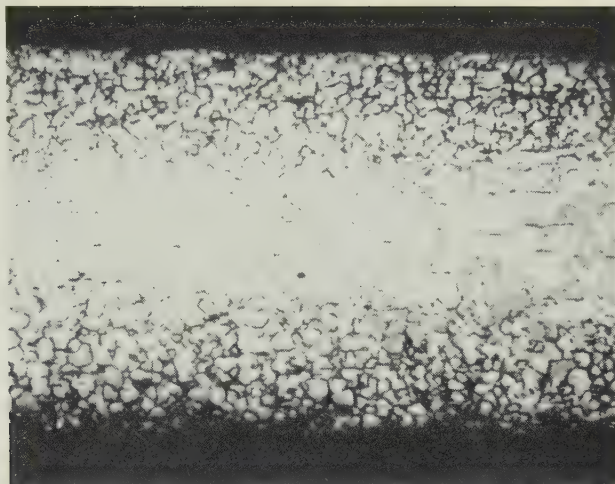


FIG. 3.—Transverse Section of a Nickel Specimen After 145 hr. in Liquid Mercury at 500° C., Showing Heavy Intercrystalline Attack.  $\times 50$ .

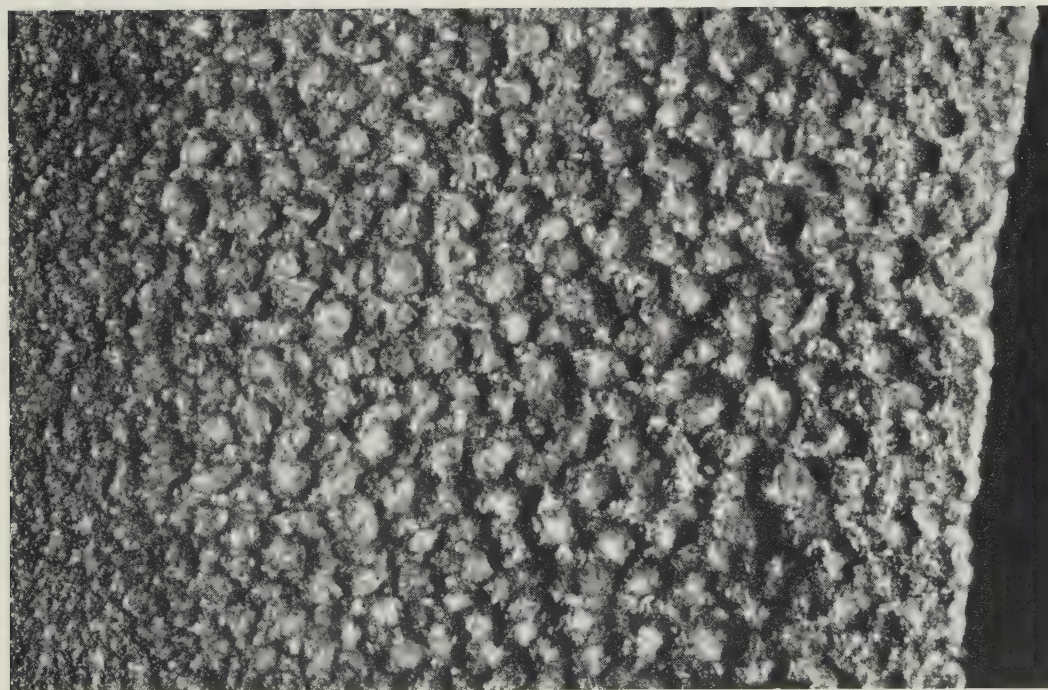
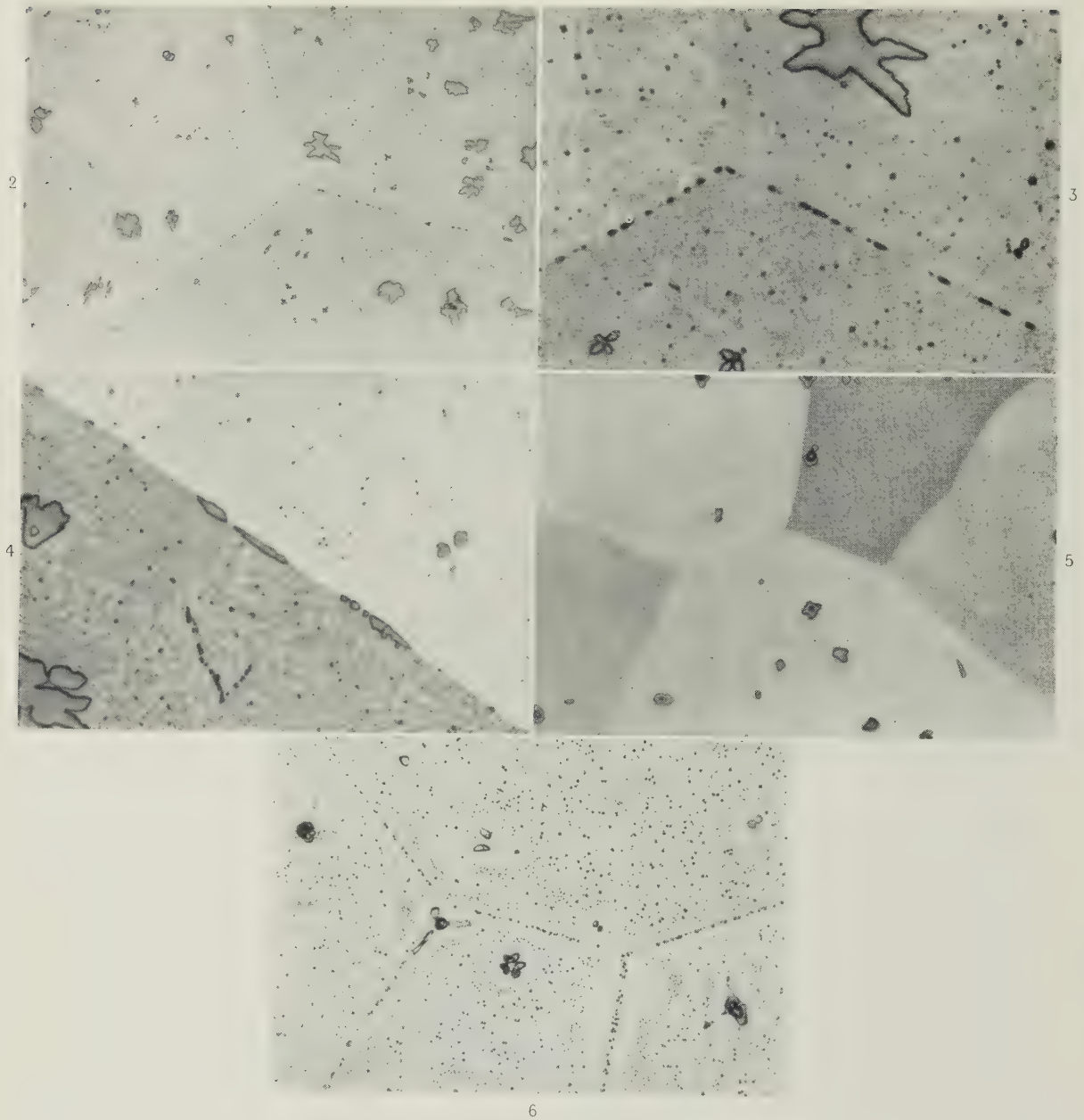


FIG. 4.—Macrophotograph of a Nickel Specimen After 88 hr. in Liquid Mercury at Room Temperature with the Probe of an Ultrasonic Generator Vibrating at 30 kc./s. Placed in Contact with It, Showing Severe Cavitation Erosion.  $\times 60$ .

TYPICAL STRUCTURES OF  $\beta$ -BRASS.



FIGS. 2-4.—As-Cast Alloy.

FIG. 2.—Showing large and fine iron-bearing constituents inside the grains and fine constituents at grain boundaries.  $\times 500$ .

FIG. 3.—Similar to Fig. 2.  $\times 2000$ .

FIG. 4.—Showing larger constituents at grain boundaries.  $\times 2000$ .

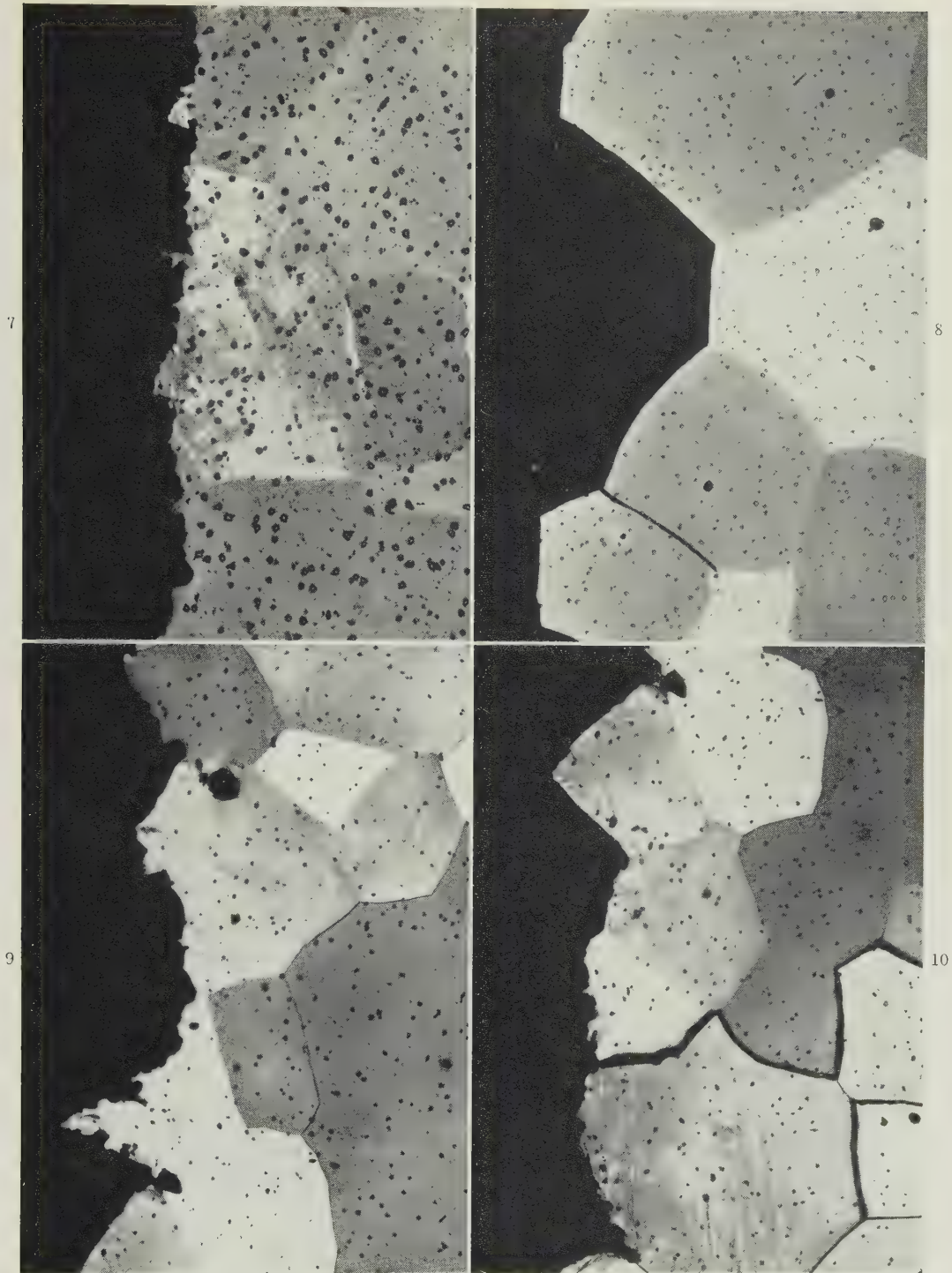
FIG. 5.—General Microstructure after 1 hr. at  $750^{\circ}\text{C}$ ., Water-Quenched.  $\times 500$ .

FIG. 6.—General Microstructure after 1 hr. at  $750^{\circ}\text{C}$ ., Air-Cooled.  $\times 500$ .

(All reduced by  $\frac{1}{2}$  in reproduction.)



TYPICAL FRACTURES OF  $\beta$ -BRASS IN THE CHARPY TEST.



FIGS. 7 and 8.—As-Cast Alloy.  $\times 75$ .

FIG. 7.—Transcrystalline fracture at room temperature, showing deformation markings.

FIG. 8.—Intercrystalline fracture at 600° C.

FIGS. 9 and 10.—Water-Quenched Alloy After 1 hr. at 750° C., Tested at Room Temperature.  $\times 75$ .

FIG. 9.—Region showing mostly transcrystalline fracture.

FIG. 10.—Region showing mostly intercrystalline fracture, with transverse intercrystalline cracks.





# THE REMOVAL OF OXIDE FROM ALUMINIUM BY BRAZING FLUXES\*

1718

By M. F. JORDAN,† B.Sc., Ph.D., STUDENT MEMBER, and D. R. MILNER,‡ M.Sc.

## SYNOPSIS

The progress of oxide removal in aluminium brazing has been followed by studying the fringe systems set up by interference of monochromatic light reflected from the metal with that reflected from any partially detached oxide. The oxide-removal times obtained for a range of fluxes of differing fluoride/chloride contents show the fluoride to be the more active constituent.

Measurements of the potential of the oxide-coated aluminium made during the course of the fluxing action show that the rate of potential decay is related to the flux efficiency. On the basis of these results, an electrochemical theory is postulated in which the oxide is undermined by the action of a cell set up between the oxide and the metal. It has been established that dissolved oxygen is essential to the fluxing action, and suggested cell reactions are  $\text{Al} = \text{Al}^{+++} + 3e$  at the anode, and  $2\text{O} + 4e = 2\text{O}^{--}$  at the cathode.

The solution potential of the aluminium in the fluxes has been measured against a reversible sodium electrode and found to fall to a limiting value as the fluoride content is increased. This has been interpreted on the basis of the electrochemical theory to account for the greater efficiency of fluxes containing fluorides.

## I.—INTRODUCTION

ALUMINIUM and its alloys are characterized by extremely tenacious oxide films, and these must be removed in brazing and welding. There are numerous fluxes that remove the oxide rapidly and effectively, and essentially these consist of mixtures of alkali-metal chlorides and fluorides with the addition of small percentages of one or two other metal halides. Many of the fluxes in commercial use are under patent, but a list of representative compositions used in brazing has been published by West.<sup>1</sup>

For many years the action of these fluxes was attributed to their ability to dissolve the oxide, until West<sup>2</sup> showed that alumina is almost insoluble in the molten flux. Further experiments with anodized aluminium strips led West to suggest that the action of the flux involved attack of the basis metal, giving mechanical detachment of the oxide film and then removal of this oxide as a suspension in the flux. This suggestion later received support from the work of Sully, Hardy, and Heal,<sup>3</sup> who showed that the water-insoluble portion of "spent" melting fluxes consists mainly of flat plates of alumina. In fact, they were able to demonstrate that this suspension of alumina is responsible for the thickening encountered with "spent" fluxes.

This detachment of the oxide was attributed by West to the formation of volatile aluminium chloride at the oxide/metal interface, as a result of the diffusion of chloride ions through the oxide film. It was known that both chlorides and fluorides were necessary to obtain effective oxide removal, and therefore he suggested that the fluorides attacked the oxide film, so permitting rapid penetration by the chloride ions. However, a consideration of the available free-energy data shows that

the reaction of aluminium with any of the chloride constituents is extremely unlikely, so that this mechanism cannot be regarded as providing an adequate explanation of the flux action. An alternative theory was advocated by Sully and his co-workers, who maintained that the oxide on molten aluminium was stripped by surface-tension forces after penetration by the flux. This explanation certainly cannot apply to the case of solid aluminium, and it is significant that the oxide is removed from both the molten and solid metal by fluxes which are identical in composition.

Thus, there is ample evidence that the oxide is detached from the aluminium, but the nature of the fluxing action remains unexplained. In the present investigation, attention has been confined to the removal of oxide from solid aluminium, as it occurs in brazing. Two techniques have been used; the first involved microscopic study of the progress of the oxide removal after fluxing, and the second consisted of measuring the potential of the aluminium during the fluxing action.

## II.—DISPLACEMENT OF THE OXIDE FILMS

The oxide films formed on aluminium are very thin, being of the order of 45 Å. at room temperature, but thickening to 1000–2000 Å. during prolonged heating at 500°–600° C.<sup>4–6</sup> Moreover, these films are transparent when in contact with metal surfaces, so that normal microscopic methods cannot be expected to be satisfactory for determining their presence or absence from the surface. It was found, however, that when the films become partially detached from an electropolished surface, they can be seen quite easily by means of the interference fringes developed by the gap between the oxide and basis metal when the specimens are viewed by

\* Manuscript received 17 February 1956.

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‡ Department of Industrial Metallurgy, Birmingham University.

monochromatic light. This effect is illustrated in Fig. 1 (Plate VIII), which shows an almost detached oxide particle on the surface of a specimen that had been immersed for a few seconds in a commercial cryolite/chloride flux.

The experimental technique involved the preparation of electropolished aluminium strips which were then oxidized, either by exposure to the atmosphere or by prolonged heating at 500° C., the thicker oxide films so produced being more suitable for many of the experiments. Specimens were partly immersed in the flux for various times, washed in water to remove the adhering flux residues, and then examined microscopically without further surface preparation. By this method, the oxide removal was studied at each stage from its initiation to ultimate completion with the cryolite/chloride flux, listed as No. 1 in Table I. The effect of flux composition was then examined by determining the time

films to establish that similar results were obtained in both cases.

### 1. THE PROGRESS OF OXIDE REMOVAL

The successive stages of oxide removal studied are illustrated in Figs. 1-4 (Plate VIII). The occurrence of the areas showing interference fringes provides further evidence that the flux action consists in the stripping of the oxide films from the aluminium surfaces. It is clear that this takes place as a result of an interfacial attack, and, under the conditions of the experiment, the films were completely removed from super-purity aluminium after about 2 minutes' immersion in the commercial flux. The attack began at a large number of sites within the metal grain, which became visible when the gap between the oxide and metal was sufficiently large to give the first fringe (Fig. 2); this occurred when the gap-width was  $\lambda/2$ , about 2000-2500 Å. with the

TABLE I.—*The Compositions of the Experimental Fluxes.*

Salt	Percentage by Weight									
	1 *	2	3	4	5	6	7	8	9	10 †
Potassium chloride †	38.6	42.75	42.65	42.25	41.75	41.5	39.75	37.6	34.2	...
Sodium chloride †	34.0	37.75	37.75	37.25	36.75	36.5	35.25	33.2	30.2	...
Lithium chloride	17.4	19.5	19.5	19.5	19.5	19.0	18.0	17.2	15.6	...
Cryolite, 3NaF.AlF <sub>3</sub>	10.0	...	...	...	...	...	...	...	...	...
Sodium fluoride	...	...	0.1	1.0	2.0	3.0	7.0	12.0	20.0	...
Lithium fluoride	...	...	...	...	...	...	...	...	...	27
Strontium fluoride	...	...	...	...	...	...	...	...	...	44
Aluminium fluoride	...	...	...	...	...	...	...	...	...	29

\* Proprietary flux.

† Analar purity.

‡ British Patent Application No. 1231 (1940).

required for complete oxide removal for a series of nine fluxes of varying fluoride and chloride contents. These fluxes were prepared by successive additions of sodium fluoride to a mixture of chlorides, as can be seen from the list of compositions given in Table I. With all these fluxes, including the cryolite mixture, it was found that when first used they produced a black precipitate on the aluminium which tended to obliterate the surface. Consequently, in order to permit the microscopic examination of the strips, the fluxes were "refined" by repeated heating in aluminium crucibles until this precipitation ceased. In most cases the working temperature of the fluxes was 610°-620° C. but with mixtures containing more than 20% fluoride it had to be increased to 645°-650° C. With the very active fluxes, short immersion times were often necessary, so that it was essential to preheat the specimens, and this was done in sealed glass tubes in order to eliminate the attack which occurred in the flux vapour.

The bulk of the experimental work was carried out with super-purity aluminium, as this contained the minimum number of surface impurities, and the specimens were prepared with oxide films formed at high temperature because these yielded much clearer interference-fringe patterns than the room-temperature films. Furthermore, the unattacked high-temperature films were appreciably coloured, so that unremoved oxide was easier to locate than in the case of the transparent films formed at room temperature. Nevertheless, sufficient experiments were made with the room-temperature

particular monochromatic light used. An idea of the distribution of these sites was obtained from Figs. 2 and 3, which showed them to be about  $10^{-4}$  cm. apart. It was noticed that, although the grain boundaries occasionally formed the initial sites of attack, more frequently they appeared to retard the removal of oxide. Further attack occurred by the expansion and linking up of the individual sites (Fig. 3), and eventually considerable areas of oxide were lifted from the surface (Fig. 4). Once appreciable patches of oxide had been released from the metal, the film buckled up and fragmented so that pieces of oxide passed into the flux. The free ends of the ruptured film frequently curled up under the compressive stresses present in the oxide, and it was possible to focus on these edges. An area illustrating this effect can be seen in Fig. 4, where the thick dark bands indicate that the gradient of the curled film was so steep that numerous fringes merged together. The final stage of the removal was reached when the bulk of the oxide film had broken up, and only small patches of oxide remained loosely attached to the surface (Fig. 1).

Similar observations were made with the oxide films formed at room temperature; here the fringes, when visible, were much closer together, indicating that the buckling was more severe. In addition, the films appeared to break away from the surface more readily (Fig. 5, Plate VIII), indicating that they were fragmenting at an earlier stage than the high-temperature films.

Oxide removal was affected quite markedly by the



purity of the metal, for it was found that the film present on commercial-purity aluminium was removed in 30 sec., as compared with 2 min. for the super-purity metal. In a number of cases, transparent triangular deposits were observed on the partially detached oxide films; these are illustrated in Fig. 6 (Plate VIII). They were confined to the oxide film and occurred only with the flux containing cryolite.

## 2. THE INFLUENCE OF FLUX COMPOSITION

The time for complete oxide removal from the electro-polished and oxidized specimens was determined for all the fluxes, and it was found that the efficiency of the flux,

TABLE II.—*The Immersion Times for Oxide Removal with the Different Fluxes.*

Flux No.	Flux Description	Oxide-Removal Time
1	Chloride + 10% cryolite	Complete after 2 min.
2	Chloride	35% complete after 2 hr.
3	Chloride + 0.1% NaF	70% " " "
4	" + 1% NaF	80% " " "
5	" + 2% NaF	Complete after 1½ hr.
6	" + 3% NaF	" " 1¼ hr.
7	" + 7% NaF	" " 20 min.
8	" + 12% NaF	" " 2 min.
9	" + 20% NaF	" " in less than 3 min.
10	Fluoride	Not determined

measured in terms of the rate of removal, depended on the fluoride content. The results are given in Table II for all the fluxes except that containing only fluorides; in this case it was impossible to examine the specimen surfaces owing to the adhering flux residues, which were almost completely insoluble. This difficulty was also experienced to a lesser extent with the 20% sodium fluoride flux, so that the time quoted can be only approximate. It is clear from these results that the fluoride is the more active constituent in these chloride/fluoride fluxes.

## 3. THE RATE AND DISTRIBUTION OF FLUX ATTACK

The rate of attack followed a general pattern for all the fluxes, the majority of the oxide being detached in a fraction of the time required to complete the removal of the entire film. A quantitative idea of the rate of the removal with a 7% sodium fluoride flux was obtained by making a visual estimate of the extent of the oxide removed after various times of immersion. This was done by scanning the surface of the aluminium strips with a microscope at a magnification of about  $\times 70$ , any doubtful areas being resolved at higher magnifications. The results, presented graphically in Fig. 7, show that, although 60% of the oxide was detached within the first 30 sec., the remainder was removed only after 20 minutes' immersion.

An examination of a large number of specimens showed that the rate of oxide removal was not uniform over the whole surface, but occurred more rapidly in the proximity of the flux surface than at lower levels in the flux. For example, the removal would be locally complete over a strip 1–2 mm. wide at the flux surface, while still in the initial stages over the rest of the immersed area. In order to examine the effect further, a specimen was bent through 90° and immersed so that its surfaces were parallel

to and just beneath the flux surface. After one minute's immersion the upper surface showed a uniform removal of 35–40%, while the lower aluminium surface showed attack only at the edges, leaving an island of unattacked oxide in the centre.

In the initial stages, the attack was confined to the whole of the oxide on individual metal grains, but later it extended in an irregular fashion to neighbouring grains. The "granular" nature of the attack was evident at all stages in the removal, and in extreme cases the oxide on one grain was completely removed while the film present on its neighbours remained intact. In addition, it was

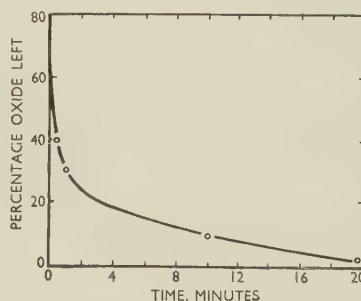


FIG. 7.—The Progress of Oxide Removal in the 7% Sodium Fluoride Flux.

noticed that remnants of oxide were left attached at the grain boundaries of the aluminium after the bulk of the film had been displaced, indicating that it was more firmly attached at these points.

## III.—CHANGES OF POTENTIAL DURING FLUXING

As a result of the microscopic examinations, it appears that the removal of the oxide film is caused by a rapid interfacial attack. It has already been pointed out that the flux action cannot be attributed to bulk reactions with the flux constituents, as these are thermodynamically unfavourable, so that some other mechanism must be sought. The very high conductivities of the single molten salts present in these fluxes indicate that they are essentially ionic,<sup>7</sup> and as in aqueous solutions of these salts a potential difference exists between the oxide and the metal, a similar situation should exist in molten fluxes. Attack may therefore occur at the oxide/metal interface by an electrochemical process.

The possibility of this type of action in the flux has been investigated in the present work. A series of electrochemical experiments were made in which the potentials of oxidized aluminium strips immersed in flux under various conditions were determined. Measurements of this nature have to be made against a standard electrode, and the one chosen was a similarly immersed oxide-free aluminium strip; this had the advantage that the observed potential decayed to zero as the oxide was removed. Thus, a technique was developed which involved the prior immersion of the reference electrode in the flux for a time sufficient to ensure complete removal of its oxide. The electrodes were in the form of strips,  $11 \times 0.25 \times 0.02$  in. which were degreased in trichlorethylene vapour before use.

Preliminary work indicated that on immersion a positive potential difference greater than 100 mV.

existed between the electrodes; this subsequently decayed so rapidly that it could be measured and recorded successfully only by the use of a cathode-ray oscilloscope and camera. Moreover, the transient character of the potential made it necessary for the immersion of the electrodes to be controlled and to be constant for all the experiments. This was accomplished by the use of a simple jig, which allowed the specimens to fall freely under gravity into the molten flux. Further, exploratory tests revealed that anomalous results were obtained when momentary solidification of the flux occurred on immersion of the specimens. Preheating of the specimen was therefore carried out, in a sealed Pyrex glass tube to prevent exposure to flux vapour.

### 1. THE ELECTROCHEMICAL POTENTIAL

The general character of the changes in the potential of the aluminium which occurred during the fluxing action was investigated with cryolite flux (the commercial mixture listed as No. 1 in Table I). Immersions were made at a flux temperature of 610°–615° C., using test electrodes with oxide films formed both at room and at high temperature. All the results were recorded as oscillograms which consisted of the experimental potential traces and a standard 50-cycle A.C. time base, and a mean potential/time curve was derived from the traces obtained for a number of immersions. It is evident from the curve for super-purity aluminium with a high-temperature oxide film shown in Fig. 8 that, on immersion of the oxide-coated electrode, a potential difference of the order of 600–650 mV. was obtained, which subsequently decayed to zero in about 40 millise.

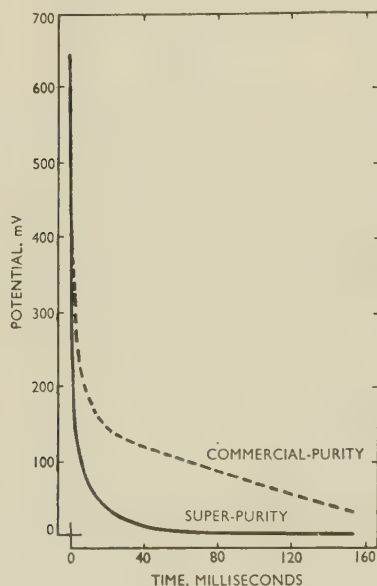


FIG. 8.—Potential/Time Curves for Super-Purity and Commercial-Purity Aluminium Using the Cryolite Flux No. 1.

The direction of this potential was constant in all the experiments in which the oxide-coated strips were positive with respect to the oxide-free strips. In addition, the decay of the potential to zero occurred in a fraction of the time required for complete removal of the oxide, which was about 1–2 min. under these conditions. There appeared to be no appreciable difference between

the results obtained with films formed at room temperature and those formed at high temperatures, but the commercial-purity aluminium with a high-temperature oxide film showed a slower decay of the potential to zero (Fig. 8).

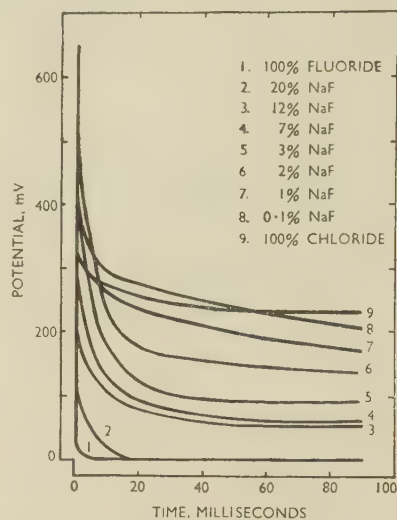


FIG. 9.—Potential/Time Curves for Fluxes of Varying Fluoride Content.

### 2. THE EFFECT OF FLUX COMPOSITION

It has been shown that, although fluxes containing only chlorides are able to remove the oxide films from aluminium, the process takes place very much more rapidly when fluoride/chloride mixtures are used. Consequently, potential/time determinations were made for the series of nine fluxes of varying fluoride content (Table I). In each case, the potential determinations were made on aluminium specimens with oxide films formed at high temperature. Owing to the higher melting points of the mixtures containing fluorides, the flux temperatures ranged between 615° and 645° C., and the immersion times for the reference electrodes were varied in accordance with the oxide-removal times quoted in Table II. An immersion time of 2 hr. was used for fluxes Nos. 2, 3, and 4, since the potential then approximated to that of a film-free strip.

Owing to the widely divergent decay times obtained with the different fluxes, the results have been plotted on two different time scales, the first in milliseconds (Fig. 9) and the other in seconds (Fig. 10). The values of the immersion potentials obtained were fairly constant at 600–650 mV. for all the fluxes except that containing only fluorides. In the latter case, a maximum value of 350 mV. was observed, but it is considered that the low value was probably not the true immersion potential, which would be difficult to ascertain owing to its extremely rapid generation and decay. The total time required for the potential to reach zero increased considerably with decreasing fluoride content, although the general shape of the curves remained unaltered. Thus, the decay time was about 2½ msec. for the 100% fluoride flux, while it was considerably more than 5 min. for the 100% chloride flux, demonstrating that the rate of potential decay is directly associated with the rate of oxide removal.

Correlation of the potential values with the degree of



oxide removal was possible only with the slow-acting fluxes. This showed, for example, that for the chloride flux after 30 sec., when the potential of the aluminium was about 200 mV., a few per cent. of the oxide had been removed, with 25% partially detached; after 5 min. the potential was that of a film-free strip, while only 5–10% of the oxide had been removed and upwards of

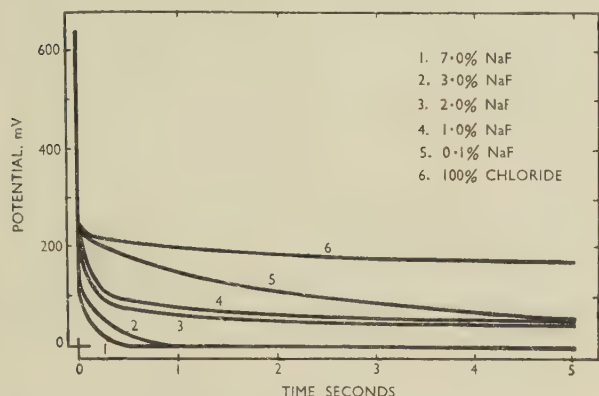


Fig. 10.—Potential/Time Curves for Fluxes of Varying Fluoride Content.

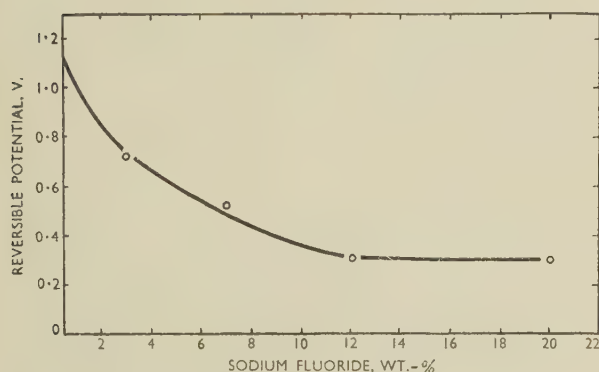


Fig. 11.—The Effect of the Sodium Fluoride Content of the Chloride/Sodium Fluoride Flux on the Solution Potential of Aluminium.

60% partially detached. However, this comparison confirmed that the potential did not drop to the value of the film-free aluminium immediately the oxide was penetrated, although the drop occurred long before the film was substantially removed.

### 3. THE EFFECT OF FLUX COMPOSITION ON THE SOLUTION POTENTIAL OF ALUMINIUM

In all the experiments so far described, the measurements were made against an oxide-free aluminium electrode, whose potential must have varied with the flux composition. Consequently, the measured values gave no indication of how the flux composition influences the electrochemical reactions; significant results for this could be obtained only by the use of a reversible electrode, the potential of which would not be markedly influenced by changes in the fluoride content of the flux. Hence, it was decided to measure, by means of a potentiometer, the potential of oxide-free aluminium in the various fluxes against a sodium electrode.

A simple cell was assembled with the molten flux as the

electrolyte and the sodium and aluminium as the electrodes. Since sodium ions diffuse quite freely through glass, a suitable reference electrode was prepared by dipping a tube containing the molten sodium into the flux, an argon atmosphere being maintained in the tube to prevent the sodium from burning away. Before each determination, the aluminium electrode was immersed for a sufficiently long time to ensure complete oxide removal before the potential was determined. Measurements were made for a 100% chloride flux and mixtures containing 3, 7, 12, and 20% sodium fluoride, and it was found that the potential of the aluminium was positive with respect to the sodium and varied with the fluoride content as shown in Fig. 11. A value of 1.125 V. was obtained for the 100% chloride flux, but this decreased rapidly with increasing fluoride content to a limiting value of 0.3 V. with 12% sodium fluoride. These values represent the true reversible potentials, for in each case, after balancing the potential, a change of  $\pm 1$  mV. caused a reversal of the cell polarity.

## IV.—THE FUNCTION OF DISSOLVED OXYGEN

The potential/time characteristics of the fluxed aluminium strips indicated that the flux action was probably electrochemical in nature. However, it was evident from free-energy considerations that the major constituents of the flux were not responsible for the cell reaction, so it was considered that the processes might involve the presence of dissolved gases, as in the aqueous corrosion of metals. In the case of metallic corrosion the principal cathodic reaction is known to involve dissolved oxygen<sup>8</sup>; the possibility of a similar reaction occurring in the flux was therefore examined by carrying out experiments with the cryolite flux, No. 1, under a vacuum and under various pressures of oxygen.

A technique was developed for degassing the flux while at the same time ensuring that the preheating and subsequent immersion of the specimen were carried out in a vacuum. The glass "cell" used in these experiments is illustrated diagrammatically in Fig. 12. Since Pyrex glass cannot withstand the pressures involved above about 400° C., an aluminium sleeve was inserted in the reaction vessel to support the glass. The aluminium specimens,  $0.4 \times 6 \times 0.02$  in., were held in a specimen tube *A* suspended inside the closed-end tube *B* by fine wire from tungsten electrodes *X* and *Z*, a long insulated flexible lead connecting the aluminium to the central electrode *Y*. Immersion of the specimens was effected by fusing the wire supporting the specimen tube, which smashed through the thin bottom of the preheating tube and plunged into the flux. A socket at *R* enabled an aluminium reference electrode to be introduced for the potential/time determinations. When it was desired to examine the extent of the oxide removal on a specimen, it was essential to prevent access of the atmosphere while the flux remained molten on the surface, so that the withdrawal of the specimens as well as their immersion had to be carried out in the vacuum. This was accomplished by means of a modified specimen head (Fig. 12), in which the specimen was attached to the tap of a large vacuum stopcock instead of to a central electrode, the tap being grooved so that, on rotation, it acted as a winch and wound up the specimen wire.

The whole system was evacuated by a single-stage vacuum pump, and the immersions were made after a vacuum had been maintained for 2 hr., the average pressure being  $1 \times 10^{-3}$  cm. Hg.

The potential/time curve obtained under vacuum is shown in Fig. 13, and comparison with the results obtained under normal conditions indicates that the shape

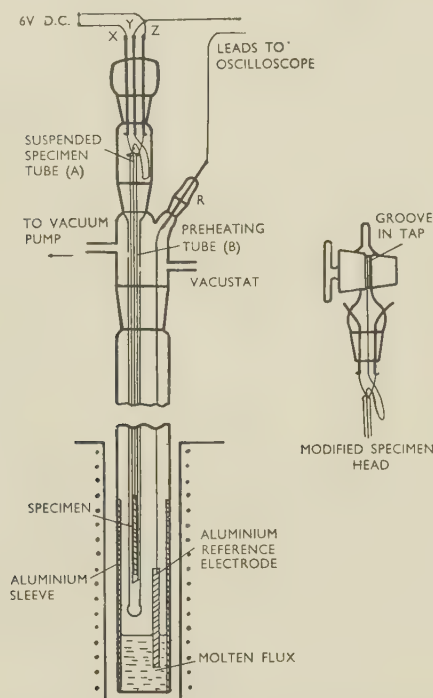


FIG. 12.—The Vacuum Apparatus Used to Determine the Effect of the Dissolved Oxygen in the Flux on Oxide Removal.

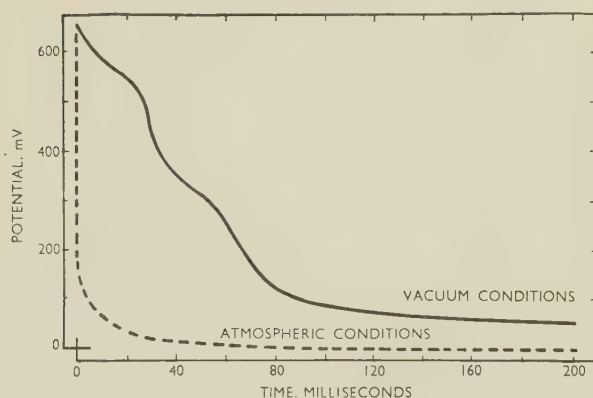


FIG. 13.—The Potential/Time Curve Obtained Under Vacuum of  $1 \times 10^{-3}$  cm. Hg with the Cryolite Flux, No. 1.

of the curve has been altered. There is no appreciable change in the potential obtained on immersion, but the subsequent decay occurs much more slowly, so that the time required for it to reach a value near zero increases from 40 to 200 millisecc. An examination after immersion for 2 min. showed that the extent of oxide removal had been reduced and corresponded to the amount removed in 2 sec. under normal atmospheric conditions.

The effect of dissolved oxygen on oxide removal was investigated more fully in a series of experiments under

vacuum and also under oxygen pressures of 1 mm. Hg and 1 atmosphere. In the experiments involving the admission of oxygen, the system was evacuated for 2 hr. and then maintained at the desired oxygen pressure for 30 min. in order to establish equilibrium with the flux. The extent of the oxide removal was then determined for various immersion times for each of the conditions, and the results are presented graphically in Fig. 14, together with those obtained under atmospheric conditions. Owing to deterioration of the surface, the determination of the area of oxide removed was more difficult for the longer immersion times; the limits of reliability have therefore been indicated at the right-hand side of the figure.

Reduction of the oxygen partial pressure below that encountered under normal atmospheric conditions decreased the rate of oxide removal, the effect increasing as the oxygen pressure was lowered from 1 mm. Hg to less than  $1 \times 10^{-3}$  cm. Hg. Furthermore, when oxygen at atmospheric pressure was admitted to the system, the removal was accelerated, so that it was complete within

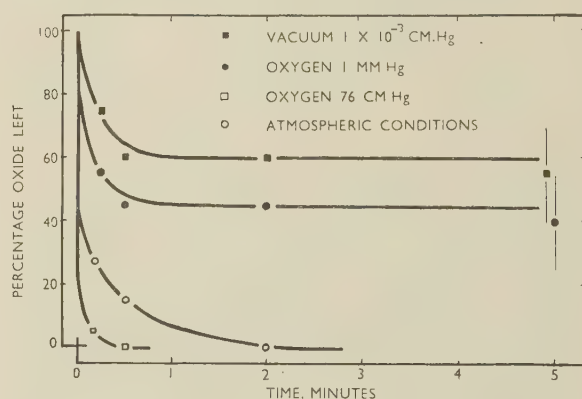


FIG. 14.—The Rate of Oxide Removal Obtained under Vacuum, Oxygen Pressures of 1 mm. Hg and 1 atmosphere, and Normal Atmospheric Conditions.

20 sec. as compared with 2 min. under atmospheric conditions. Consequently, it is evident that oxide removal is dependent on the oxygen content of the flux and the atmosphere above it. Similar experiments involving the admission of nitrogen after evacuation did not show this effect, the result with nitrogen at atmospheric pressure being little different from that obtained under vacuum.

## V.—DISCUSSION

Examination of the electropolished and oxidized aluminium strips after various times of immersion in fluxes has established that the fluxing action involves the stripping of the oxide from the basis metal. Furthermore, it has been shown that immersion in the flux also results in a rapid decay of the potential of the aluminium relative to that of a film-free strip. From the results obtained with the various flux compositions, it is evident that the potential does not fall instantaneously when the oxide is penetrated, and in fact the rates of decay are shown to decrease with the lower rates of removal. These considerations indicate that the potential movements are related to the break-up and removal of the oxide, and in fact the removal of the oxide can be



attributed to electrochemical action between the oxide and metal as will be demonstrated later in this discussion.

The stripping of the oxide from the metal can then be readily explained in terms of the postulated electrochemical action. Aluminium at the interface goes into solution in the flux, so that the oxide becomes progressively undermined, and since the film is under compression (the oxide: metal volume ratio being greater than one), once it is released from the metal it buckles and lifts from the surface. When the buckling of the film becomes severe, the brittle oxide breaks up and the particles pass into the flux as a suspension. As the area of exposed metal increases, it is to be expected that there will be a smaller tendency for the attack to be concentrated at the oxide/metal interface, with a correspondingly lower rate of undermining and hence of oxide removal. In fact, this has proved to be the case, for in all the fluxes examined the rate of attack was rapid at first but later became much slower as the oxide removal progressed (this is shown in Fig. 7 for the 7% NaF flux).

### 1. THE ELECTROCHEMICAL PROCESSES OCCURRING IN THE FLUX

Information about the nature of the electrochemical processes occurring in the flux can be obtained by a more detailed consideration of the potential/time curves. Thus, the fact that in every case the potential had fallen to the value of the film-free metal long before oxide removal was complete, indicates that the polarization of the processes occurring at the oxide must be much more severe than that at the metal. The anodic reaction, which is that occurring at the exposed metal, is simply the solution of aluminium, and can be expressed in the following way:  $\text{Al} = \text{Al}^{+++} + 3e$ . This is the reaction responsible for undermining the oxide, and does not suffer much polarization. The cathodic reaction cannot involve any of the major constituents of the flux, because the alkali metals sodium, potassium, and lithium are more electronegative than aluminium and will not discharge cathodically on the oxide film. Confirmation of this was obtained when the potential of aluminium was measured against a sodium electrode. Although, on the addition of sodium fluoride, the potential dropped to 0.3 V., the aluminium was always more cathodic than the sodium. Consequently, any electrochemical processes occurring at the cathode must involve the participation of trace constituents in the flux. In fact, the experimental results have established that the presence of dissolved oxygen is essential for oxide removal, for the rate of removal has been shown to be dependent on the oxygen pressure above the flux. The cathodic process is therefore the ionization of oxygen ( $2\text{O} + 4e = 2\text{O}^{--}$ ), and it is known that this reaction suffers severe polarization.<sup>9</sup> The more rapid rate of removal which invariably occurred at the flux/air level under atmospheric conditions is then attributable to the greater availability of oxygen as a result of diffusion from the flux surface.

### 2. THE FUNCTION OF THE FLUORIDE ION

The marked dependence of the rate of oxide removal on flux composition has indicated that the fluoride is the more active constituent of the flux. In addition, measurements made against a reversible sodium electrode showed that the effect of the fluoride constituent

was to lower the potential of the aluminium. This increased efficiency of the fluoride fluxes can be explained in terms of the electrochemical theory advanced to explain the flux action, and can best be appreciated from a consideration of the polarization curves. The cathodic process involves the ionization of oxygen, so that its polarization curve will be of the shape *CP* shown in Fig. 15.<sup>9</sup> Anodic polarization will not be severe and will correspond to a very shallow curve *AP*. To facilitate the consideration of the rate of attack, the polarization curves are plotted against current for constant anodic and cathodic areas. Then the current flowing in the cell will be represented by the intersection of the two polarization curves. When the anodic polarization curve corresponds to that at *A*, the current and hence the rate of attack will be represented by *P*. Clearly, if the anodic potential is lowered to a value *A'*, the rate of

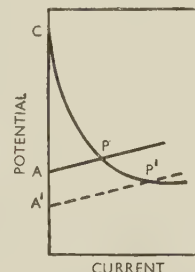


FIG. 15.—Derivation of the Rate of Attack from Polarization Curves.

attack advances considerably to a value *P'*. In fact, for a constant cathodic curve, the rate of attack increases progressively as the anodic potential is lowered. Thus, it can be appreciated that, since the addition of fluoride lowers the solution potential of the aluminium, it also results in an increased rate of attack. The effect of the fluoride additions on the aluminium potential can probably be attributed to the formation of the stable complex  $\text{AlF}_6^{---}$  which results in a lowering of the number of free aluminium ions present in the flux.

An interesting feature observed only with the flux containing cryolite was the presence of small triangular deposits on the partially detached oxide (Fig. 6, Plate VIII). These were completely insoluble in water, and it seems probable that they were small crystals of aluminium fluoride resulting from the slight dissociation of the cryolite. Their presence on the oxide can be attributed to the suitability of the surface for the nucleation and subsequent growth of the crystallites.

### 3. THE INITIATION OF THE FLUX ATTACK

The first stage in the removal of the oxide must be the penetration of the film, for until this has occurred there can be no undermining action at the oxide/metal interface. Since removal of oxide took place in fluxes containing all chlorides or all fluorides, both the fluoride and the chloride ions must be capable of penetrating the films. Moreover, the sharp fall of potential observed immediately on immersion of the oxide-coated aluminium in all the fluxes indicates that penetration by both ions occurs almost instantaneously.

Examination of the oxide films in the very early stages of attack has shown that the lifting sometimes begins at the grain boundaries of the aluminium, but

more frequently it starts at a large number of individual sites within the metal grains. These initial sites of attack, which were about  $10^{-4}$  cm. apart, may have originated at inhomogeneities in the oxide film. Little is known about the type of defect that can exist in these films, but the dislocations in the oxide arising from lattice misfit at the oxide/metal interface may be adequate to permit diffusion of the flux anions.

A distinctive feature of the flux action was that the attack progressed in a "granular" fashion, being uniform over each individual metal grain but varying from one grain to another. This may be attributable either to different degrees of misfit between the metal and the oxide or to differences in the electrode potential of the aluminium grains due to variation in their orientations.

#### 4. SOME PRACTICAL IMPLICATIONS

In the present investigation, attention has been confined to the mechanism of oxide removal from solid aluminium by brazing fluxes, and no attempt has been made to study the influence of factors arising from the brazing processes. It would appear, however, that some of the results obtained have practical significance. Thus, there can no longer be any doubt that the most efficient of the alkali-metal halide fluxes are those which contain appreciable quantities of fluoride. However, the variation of the solution potential of aluminium with flux composition has shown that little advantage is gained by addition of more than 12 wt.-% of sodium fluoride, which therefore represents the minimum fluoride content giving efficient oxide removal. This is clearly of importance in aluminium brazing, where working temperatures must not rise much above  $600^{\circ}\text{C}$ ., because the melting point of the flux increases with the fluoride content.

The oxide-removal times determined for the various fluxes were mean values for the whole of the surface of the strip immersed in the flux and cannot be applied directly to practical brazing conditions. Nevertheless, the fact that the rate of oxide removal at the flux/air level was much greater than that in the body of the flux is of considerable significance. The conditions at the flux/air level would correspond to torch-brazing and those in the body of the flux to dip-brazing, so that oxide removal would be expected to occur more rapidly in the former case owing to the greater availability of oxygen.

The mechanism of oxide removal postulated leaves some doubt about the efficiency of the flux in preventing further oxidation once the original oxide film has been removed. Thus, if sufficient oxygen is present in the flux to effect removal of the original oxide film, there is no obvious reason why oxygen should not continue to diffuse through the flux causing further oxidation. This may, in fact, be the underlying reason for the relatively poor flow properties characteristic of the aluminium-brazing process when compared with brazing processes in other flux/metal systems.

Finally, it is considered that, although the whole of the present investigation has been concerned with the fluxing of solid aluminium as it occurs in brazing, the results may well have a direct bearing on fluxing action in the welding and melting of aluminium and its alloys.

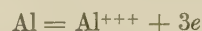
#### VI.—CONCLUSIONS

(1) Studies carried out by the interference-fringe technique have confirmed that the oxide films on aluminium are not dissolved, but are detached from the surface by the flux.

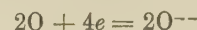
(2) The oxide-removal times obtained for a range of fluxes of differing chloride/fluoride contents have shown that the fluoride is the more active constituent.

(3) The oxide film is undermined as a result of electrochemical action at the oxide/metal interface, a cell being set up between the oxide and metal.

(4) The processes occurring in this electrochemical cell involve the presence of dissolved oxygen in the flux, the reaction at the metal as anode being:



and that at the oxide as cathode:



(5) The increased efficiency of the fluxes containing fluorides compared with those containing only chlorides is due to an increase in the potential available for the cell reaction. This results from a lowering of the solution potential of the aluminium, probably as a consequence of the formation of the stable  $\text{AlF}_6^{---}$  ion.

#### ACKNOWLEDGEMENTS

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# THE RELATION DURING CREEP BETWEEN GRAIN-BOUNDARY SLIDING, SUB-CRYSTAL SIZE, AND EXTENSION\*

1719

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(Communication from the National Physical Laboratory)

## SYNOPSIS

Creep tests have been carried out on copper, iron, cadmium, zinc, tin, aluminium alloy R.R.58, and a copper-0.37 wt.-% beryllium alloy, each at one temperature, and on super-pure aluminium at several temperatures in the range 100°–500° C. The object was to test two relations previously found with super-pure aluminium at 200° C., namely: (i) that the ratio (grain-boundary sliding)/(elongation), which has the dimensions of length, remains virtually constant throughout any one creep test, and (ii) that it is related to the size of the sub-crystals which form during creep. The former relation, but not the latter, was found to hold in all the present tests. These and other recent results suggest a new mechanism for grain-boundary sliding, which is outlined.

## I.—INTRODUCTION

RESULTS of previous creep tests on aluminium at 200° C. had shown that the ratio (average distance of grain-boundary sliding)/(total elongation) remained constant throughout any given test and was closely related to the diameter of the sub-crystals into which grains broke down during creep.<sup>1</sup> The investigation now described was carried out to ascertain whether the same relationship holds for other metals and for aluminium at other temperatures. Tests have been made on five pure metals other than aluminium, crystallizing in four different systems, on two alloys, and on pure aluminium over the temperature range 100°–500° C.

## II.—EXPERIMENTAL DETAILS

Data regarding the metals used are contained in Table I. In order to produce a surface free from work-hardening, the specimens were given the heat-treatments listed in the table immediately before the final electropolish, except in the case of the copper-beryllium alloy and the R.R.58 aluminium alloy, which had already been heat-treated when received. The copper-beryllium specimen was rubbed on emery paper and electropolished, but the 1½-in.-dia. aluminium-alloy bar had to be machined to produce a ¼-in.-thick specimen. This specimen was hand-polished and finally given a flash electropolish. Except for these two specimens, gauge lines were scribed before annealing.

Specimens were tested under constant load in vacuum or in air, as indicated in Table II. The vacuum seal around the sliding shackle was of the Wilson type and introduced negligible friction.<sup>2</sup> Specimens were periodically removed from the creep machine for measurement of elongation and grain-boundary sliding. With the exception of the R.R. 58 alloy, four gauge marks had been scribed on each specimen, dividing the gauge-

length into three zones each about 0.4 in. long, and measurements were made separately in each zone, in case necking occurred towards the end of a test. On the R.R.58 specimen eleven gauge marks, 0.1 in. apart, were scribed, for reasons explained later. The components of the displacements normal to the surface were measured at about 40 grain boundaries in each zone, and from the average value the mean total displacement was calculated by a simple averaging procedure. Necking occurred in copper, iron, and the R.R.58 alloy. The results quoted for copper and iron exclude the necked zone.

As preliminary tests showed that the initial creep rate was sometimes very fast, a preliminary "run" was made which lasted a very short time, e.g. 1 min., and the first measurements were then carried out. To minimize strain during the heating period, which usually lasted about 1½ hr., for short runs the specimen was loaded as soon as the correct temperature had been reached, without waiting for temperature equilibrium to be attained. Not more than 15 min. elapsed with the specimen within 10° C. of the test temperature before the load was applied. During the heating period, the load was supported in such a way that the residual load on the specimen was only a few ounces.

The tapered specimens of pure aluminium (Table I) were used to check some of the results obtained with the parallel-sided specimens. They had a gauge-length of about 2½ in., which tapered from ¾ in. wide at one end to ⅜ in. at the other, and were scribed at 1-cm. intervals. Each specimen was loaded for 100 hr. at a temperature in the range 100°–500° C., the load being such as to cause 10% extension or more at the narrow end and about 1% at the wide end. Elongations were measured between each pair of scribed lines, and grain-boundary sliding was measured in the vicinity of each line. By this means the amount of sliding for a particular elongation, e.g. 10% in 100 hr., could be determined by interpolation, and by

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sectioning at the corresponding position along the specimen, the sub-crystal size produced by this rate of extension could be ascertained.

### III.—EXPERIMENTAL RESULTS

The average of the measured grain-boundary sliding is plotted against the total elongation of the specimen in Fig. 1 for cadmium, iron, tin, and zinc, and in Figs. 4, 7, 9, and 12 for the copper-beryllium alloy, the R.R.58 alloy, aluminium, and copper, respectively. With the

exception of copper, which showed relatively small deviation from linearity, the points in every case are well represented by a straight line, and the rule that during creep the rate of grain-boundary sliding is proportional to the rate of total elongation is therefore quite widely applicable. The data for all the tests are summarized in Table II, from which it is seen that the ratio of the elongation due to grain-boundary sliding to the total elongation (column 7) varied considerably from metal to metal. It is necessary to describe in detail only those tests which exhibited features of special interest.

TABLE I.—Data Regarding Starting Material and Specimens

Metal	Initial Condition	Annealing Treatment	No. of Grains/mm.*	Nominal Dimensions of Gauge-Length, in.
Copper (O.F.H.C., 99.98%)	Cold-rolled strip, $\frac{1}{8}$ in. thick	2 hr. at 750° C. <i>in vacuo</i> , furnace-cooled to room temperature	11.5	$1\frac{1}{4} \times \frac{3}{8} \times \frac{1}{4}$
Iron (99.97%)	Hot-pressed slab, $\frac{1}{8}$ in. thick	$\frac{1}{2}$ hr. at 950° C. in air, furnace-cooled to room temperature	3.0	
Cadmium (99.95%)	Cold-rolled strip, $\frac{1}{8}$ in. thick	1 hr. at 200° C. in oil, air-cooled to room temperature	3.9	
Zinc (99.99+%)	" " "	1 hr. at 250° C. in oil, air-cooled to room temperature	35.2	
Tin ("Chempur" 99.99%)	" " "	1 hr. at 150° C. in air, air-cooled to room temperature	0.8	$1 \times 0.28 \times \frac{1}{4}$
Aluminium alloy R.R.58	Extruded bar, $1\frac{1}{8}$ in. dia.	20 hr. at 530° C., quenched into boiling water, tempered 20 hr. at 200° C.	7.3	
Copper-0.37 wt.-% beryllium alloy	Cold-rolled strip, $\frac{1}{16}$ in. thick	2 hr. at 950° C., quenched	2.4	$1\frac{1}{4} \times \frac{3}{8} \times \frac{1}{16}$
Aluminium (super-pure 99.98%)	Cold-rolled strip, $\frac{1}{8}$ in. thick	2 hr. at 500° C., furnace-cooled to 200° C., air-cooled to room temperature	3.13 (parallel-sided specimens) 2.73 (tapered specimens)	$1\frac{1}{4} \times \frac{3}{8} \times \frac{1}{4}$

\* Number of grains intercepted by a line 1 mm. long parallel to the length axis of the specimen.

TABLE II.—Experimental Data and Results

Material	Tested in :	Temp. of Test, ° C.	Duration of Test, hr.	Initial Stress, tons/in. <sup>2</sup>	Final E%	E%g.b. ÷ E%	Sub-Crystal Dia. d, mm.	Sliding $\frac{E\% - E\%g.b.}{mm.}$	Fractured	No. of Grains/ mm.
Copper (O.F.H.C.) .	Vacuum	400	318	1.3	5.6	0.50	...	0.12	Yes	11.5
Iron (99.97%) . . .	"	550	5½	2.5	10.4	0.14	...	0.079	"	3.0
Cadmium (99.95%) .	"	100	51	0.616	20.2	0.46	0.013	0.34	No	3.9
Zinc (99.99+%) . .	"	150	387	0.446	24.5	0.77	...	0.097	"	35.2
Tin (99.99%) . . .	Air	r.t.	74½	0.214	23.4	0.051	0.22	0.095	"	0.8
Aluminium alloy R.R.58	"	250	264½	7.0	1.8*, 9.6†	0.13	...	0.031	Yes	7.3
Copper-0.37 wt.-% beryl- lium alloy . . . . .	Vacuum	400	327	3.5	5.6	0.27	...	0.21	"	2.4
		100	330	1.4	18.4	0.027	...	0.014		
		300	300	0.183	21.6	0.25	0.096	0.13		
		350	140	0.10	20.8	0.33	0.20	0.19		
Aluminium (99.98%) .	Air	400	205½	0.068	22.2	0.38	0.25	0.23	No	Mean was 3.13
		100	100	0.072	22.1	0.25	0.30	0.15		
		450	187	0.049	18.5	0.34	0.34	0.23		
		110	0.051	18.4	0.26	0.33	0.16			
At position along specimen where elongation was 10%										
Tapered aluminium speci- men (99.98%) . . . .	Air	100	100	1.61	10	0.012	...	0.0062	No	Mean was 2.73
		150	100	0.80	10	0.054	...	0.03		
		200	100	0.57	10	0.095	0.061	0.054		
		250	100	0.32	10	0.16	0.064	0.096		
		300	100	0.172	10	0.20	0.12	0.12		
		350	100	0.104	10	0.19	0.23	0.12		
		400	100	0.074	10	0.20	0.24	0.13		
		450	100	0.058	10	0.18	~0.6	0.11		
	500	100	0.0414	10	0.21	~0.6	0.14			

\* Uniform elongation.

† Elongation in a length of  $\frac{1}{8}$  in. containing the fracture.



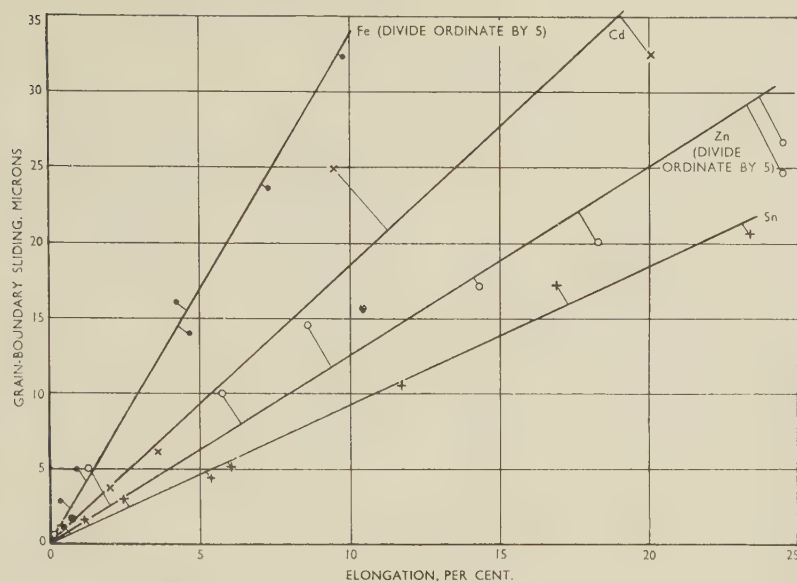


FIG. 1.—Plot of Grain-Boundary Sliding Against Elongation for Cadmium, Iron, Tin, and Zinc.

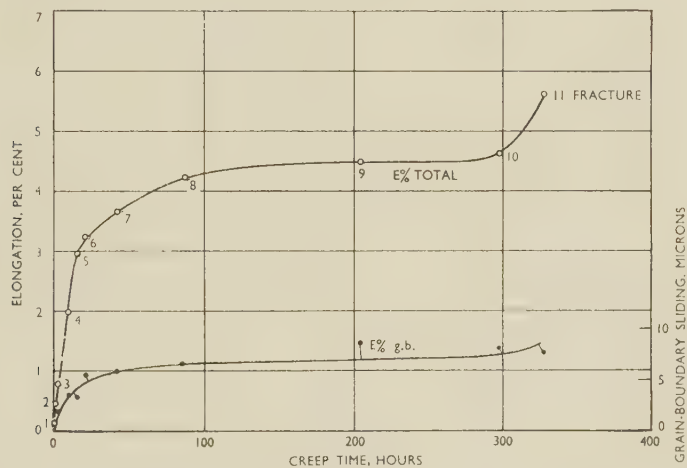


FIG. 2.—Creep Elongation/Time Curves for Copper-Beryllium Alloy Specimen Extended at 400° C. Under an Initial Stress of 3.5 tons/in.<sup>2</sup>.

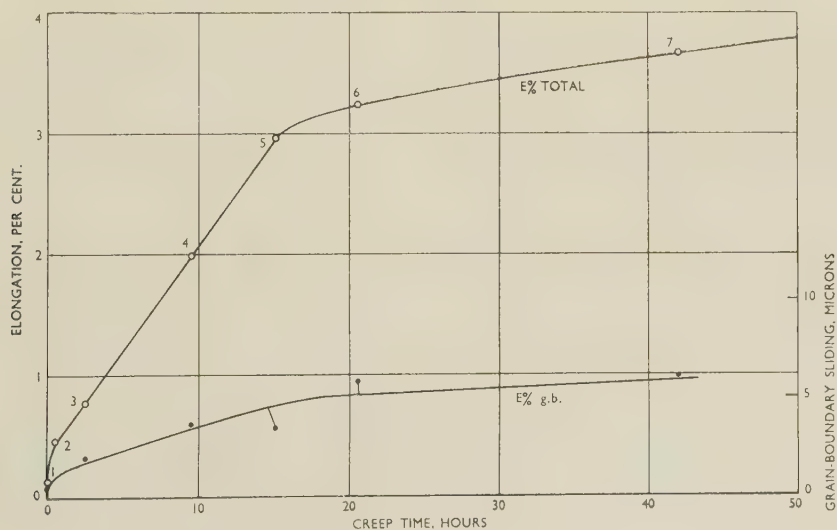


FIG. 3.—Initial Portions of Curves in Fig. 2 Plotted on a Larger Scale.

## 1. COPPER-BERYLLIUM ALLOY

The elongation/time curve up to fracture is plotted in Fig. 2. In the same figure the grain-boundary sliding/time curve is plotted with the right-hand ordinate scale so chosen that the elongation due to sliding calculated from the equation:

$$E_{\text{og.b.}}^{\circ} = \frac{100n\bar{p}}{\sqrt{2}} \quad (1)$$

(where  $n$  is the number of grain boundaries intersected by a line 1 cm. long parallel to the stress axis and  $\bar{p}$  is the mean total displacement at grain boundaries) is given by the ordinate scale on the left. An interesting feature is that after about 20 hr. the creep rate fell to a new, considerably lower rate. That this was not the ordinary transition from primary to secondary creep can be seen from Fig. 3, in which the initial portions of the

that the rate of grain-boundary sliding is controlled by the rate of grain deformation.

## 2. R.R.58 ALUMINIUM ALLOY

Preliminary tests on R.R.58 alloy showed that, outside the region in which there was marked necking, the elongation was small. To obtain data for larger deformations it was therefore necessary to make some measurements in the necked region. In order that these measurements should relate to reasonably uniform conditions, the 1-in. gauge-length was divided into sections only 0.1 in. long; measurements of extensions over such short distances were made with a sensitive travelling microscope. The 1-in. gauge-length was reduced in width by 0.02 in. compared with the rest of the 2-in. parallel portion to ensure that fracture would occur within it.

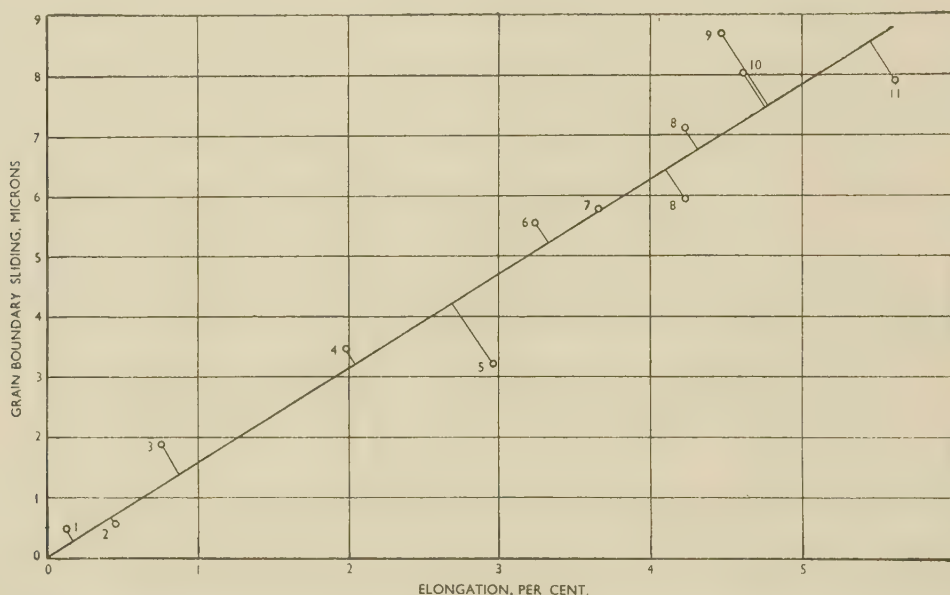


FIG. 4.—Plot of Grain-Boundary Sliding Against Elongation for Copper-Beryllium Alloy (same specimen as in Fig. 2).

creep curves are plotted on an enlarged time scale. The figure shows that the ordinary primary stage of creep was complete in about 1 hr. Sliding also decelerated after about 1 hr. and again after about 20 hr. This can best be seen, as far as the first deceleration is concerned, from Fig. 4, in which sliding is plotted against total elongation. Although the measurements of sliding were not sufficiently accurate to ensure that the proportionality between sliding and elongation was exactly the same before and after each deceleration, they were good enough to show that any change was not greater than  $1\frac{1}{2}:1$ , which is small compared with the changes in the rate of extension. These were quite large: extension during the first minute (up to point 1) was at the rate of 720% in 100 hr., between the first and second decelerations (point 3—point 5) at the rate of 10% in 100 hr., and after the second deceleration (point 9—point 10) at the rate of 0.15% in 100 hr.; that is, in the ratio 5000:70:1. In the discussion (p. 48), the relative constancy of the ratio (sliding)/(elongation) in this specimen is used as evidence

Elongation is plotted against time in Fig. 5 for the whole 1-in. gauge-length and also for the regions marked *A* and *C* in the inset. The extension was fairly uniform along the specimen up to about 1% elongation, but after that it became very uneven. In Fig. 6 the elongation due to sliding is plotted against time and shows a similar behaviour. Consequently, in the plot of sliding against total elongation in Fig. 7, average values for the whole 1-in. gauge-length are plotted only up to 1% extension (point 4) and separate values are plotted for the regions *A*, *B*, and *C*, which, individually, behaved in a reasonably uniform way. All the points are well fitted by a single straight line, including even the last two for region *C* in which fracture occurred, plotted in the inset graph in Fig. 7 (the straight line in this graph has the same slope as that in the main graph). Thus, the same proportionality between sliding and elongation is maintained for a wide range of rates of elongation; for example, the mean rate during the first 200 hr. (up to point 2) was 0.06%/100 hr., while the mean rate towards the end of



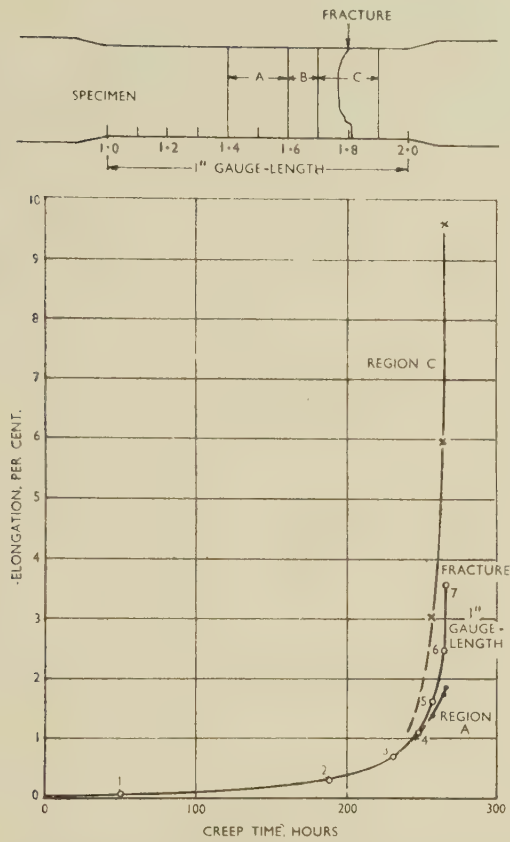


FIG. 5.—Creep Elongation/Time Curve for R.R.58 Aluminium Alloy Specimen Extended at 250° C. Under an Initial Stress of 7 tons/in.<sup>2</sup>.

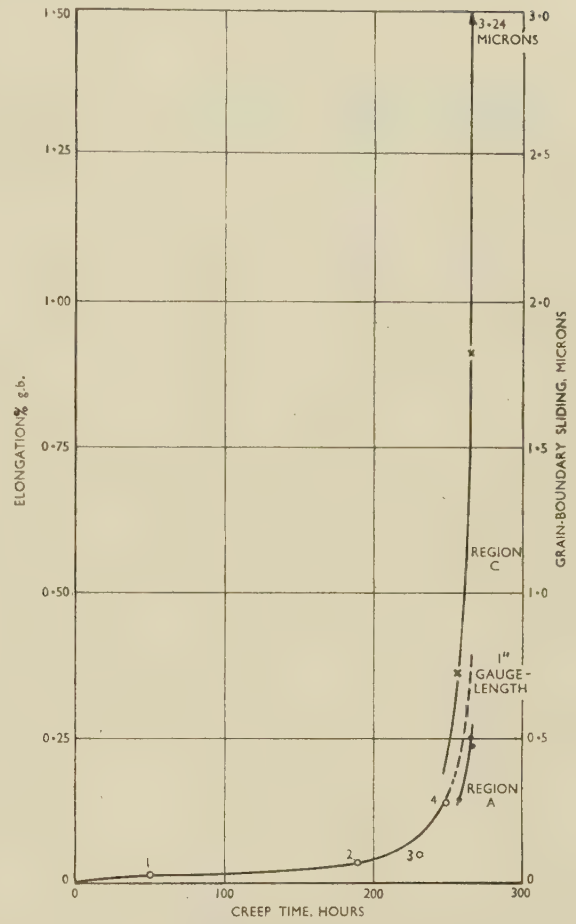


FIG. 6.—Creep Elongation (Grain Boundary)/Time Curves for Same Specimen as in Fig. 5.

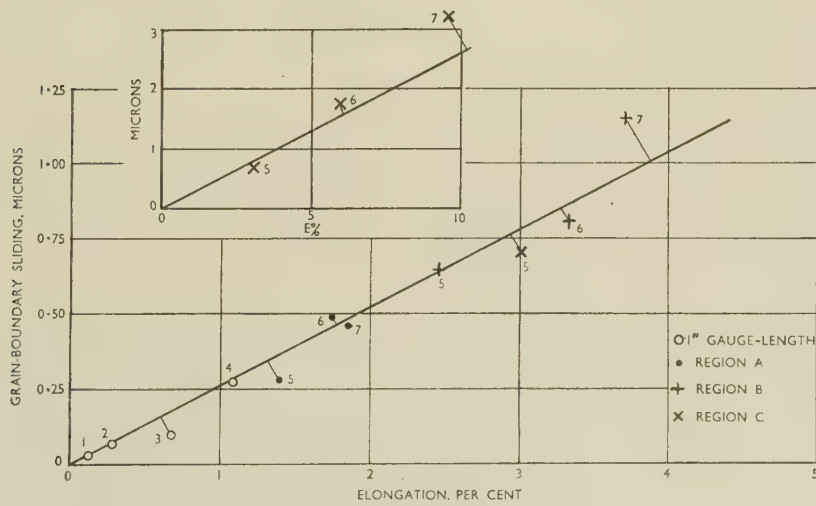


FIG. 7.—Plot of Grain-Boundary Sliding Against Elongation for Same Specimen as in Fig. 5.

tertiary creep in region *B* (between points 5 and 7) was 14%/100 hr., i.e., about 250 times greater.

### 3. PURE ALUMINIUM

Curves of creep elongation against time for the lowest (100° C.) and highest (450° C.) temperature at which such tests were made are plotted in Fig. 8, and grain-boundary

generally believed to be greater the higher the temperature for a given rate of extension. The data in Table II show, however, that the ratio  $E_{\text{g.b.}}^{\circ}/E_{\text{total}}^{\circ}$  for these specimens does not increase above 350° C. It fluctuates around 0.3, and the fluctuations can readily be traced to unavoidable variations in the rate of extension, an increase in the rate, of course, reducing the ratio. The constancy above 350° C. is shown more clearly in Fig. 10

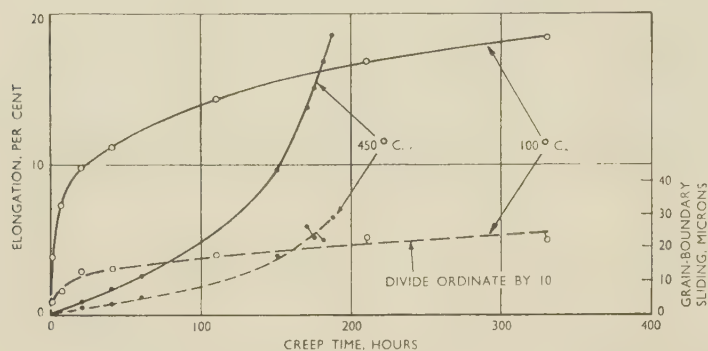


FIG. 8.—Creep Elongation/Time Curves for Super-Pure Aluminium.

KEY  
 ——— Measured elongation.  
 - - - Elongation due to sliding at grain boundaries.

FIG. 9.—Relation Between Grain-Boundary Sliding and Elongation for Specimens of Fig. 8.

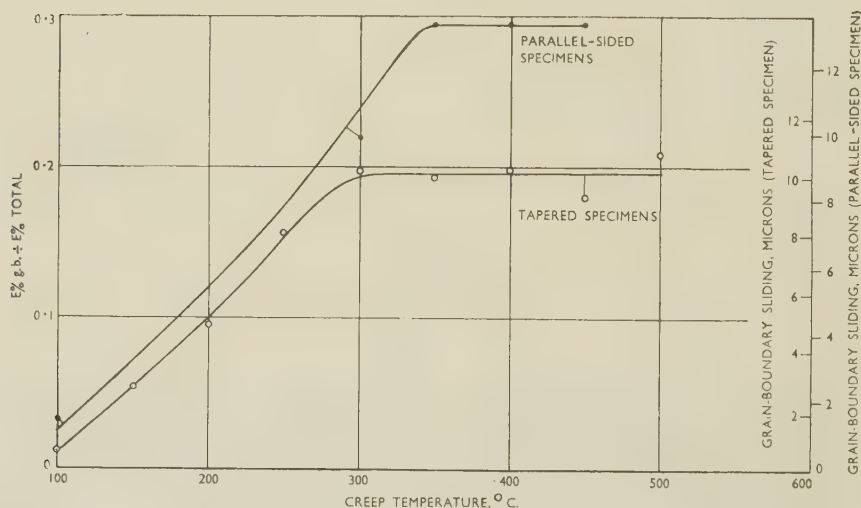
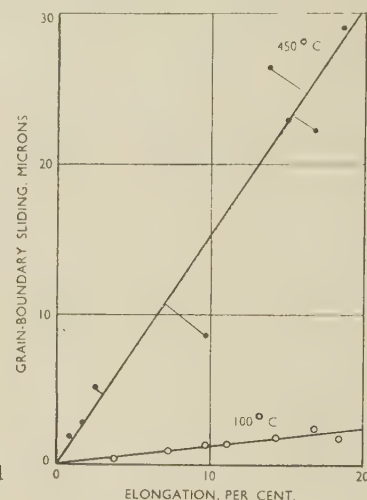


FIG. 10.—Variation of  $E_{\text{g.b.}}^{\circ} \div E_{\text{total}}^{\circ}$  with Test Temperature in Aluminium, for a Creep Extension of 10% in 100 hr.

sliding is plotted (as in Fig. 2) in such a way that the ordinate scale on the left indicates the elongation due to sliding. At 100° C. there was much primary creep, while at 450° C. primary creep is not detectable on the scale plotted and tertiary creep soon set in, incidentally without visible necking. In both tests, however, sliding was proportional to elongation within the limits of experimental error as shown in Fig. 9. At intermediate temperatures this was also the case.

An unexpected feature is worth mentioning. The amount of sliding in relation to grain deformation is

(upper curve), in which the ratio is plotted against temperature for a constant rate of extension, the compensation for this rate being made at 100° and 300° C. with the help of the rate-sensitivity of the tapered specimens referred to below. This constancy above 350° C. signifies that sliding does not continue to increase in relation to grain deformation above that temperature.

As this result ran counter to accepted opinion, a check was deemed desirable, and it was chiefly for this purpose that the tests on the tapered specimens were made, since with this form of specimen there was no difficulty in



closely straddling a chosen rate of 10% extension in 100 hr. As the further data in Table II show, the ratio  $E_{\text{og.b.}}^{\circ}/E_{\text{total}}^{\circ}$  did not increase above 300° C. for the tapered specimens. This set of results is also plotted in Fig. 10 (lower curve).

Finally, a few tests were made on specimens of aluminium, nominally the same in composition, but cast to ingot on a different occasion. Unfortunately, sufficient material was available for only three tests, at 300°, 400°, and 500° C., and the rates of these varied considerably. Correcting by the rate-sensitivity of the tapered specimens gave a ratio  $E_{\text{og.b.}}^{\circ}/E_{\text{total}}^{\circ}$  which increased continuously with temperature instead of following the plateaux shown in Fig. 10. The strips used for the parallel-sided and tapered specimens, although coming from one ingot, were rolled separately

Fig. 11) was 707% in 100 hr. and later (points 4-7 in Fig. 11) was 0.76% in 100 hr., a change of nearly 1000 : 1, while the ratio (sliding)/(elongation) changed by only 1 : 3.

### 5. SUB-CRYSTALS

After the creep test, each specimen was sectioned and the section examined microscopically, and sometimes with X-rays, for sub-crystals. A clear sub-crystal structure was found only in cadmium, tin, and aluminium. Iron is known to break up into sub-crystals during creep,<sup>3</sup> but the sub-crystals formed in the present case were too ill-defined for their size to be measured, probably because this test was a particularly rapid one. Zinc also is known to break up into sub-crystals during creep,<sup>4</sup> but X-ray examination of the present specimen

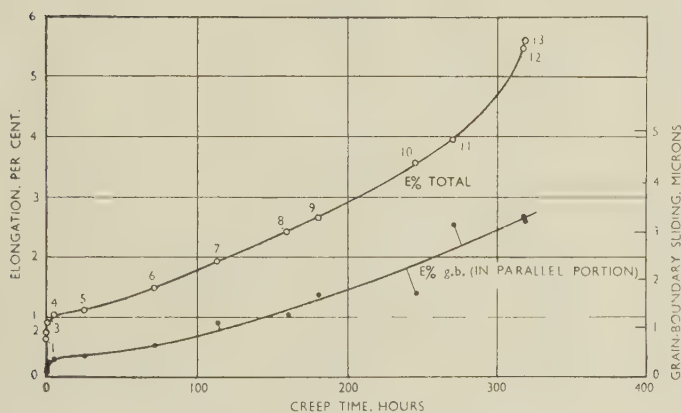


FIG. 11.—Creep Elongation/Time Curves for Copper Specimen Extended at 400° C. Under an Initial Stress of 1.3 tons/in.<sup>2</sup>.

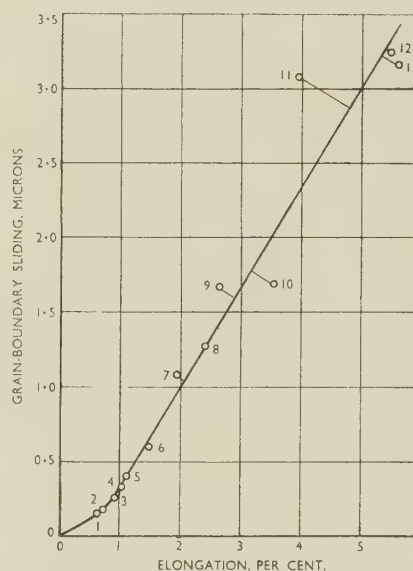


FIG. 12.—Plot of Grain-Boundary Sliding Against Elongation for the Same Specimen as in Fig. 11.

and probably with minor differences in rolling schedules which presumably might be responsible for the difference of 50° C. in the temperature at which the plateaux start. It appears, therefore that this temperature may be highly sensitive to structure and impurities.

### 4. COPPER

The curves for copper are reproduced to illustrate the one test in which a deviation from constancy in the sliding/elongation relationship was found that lay indisputably outside experimental error. The elongation/time and grain-boundary sliding/time curves are plotted in Fig. 11 and the sliding/elongation curve in Fig. 12. In the latter the slope up to 0.7% extension is less steep than later on; this behaviour was repeated in a duplicate test. However, the change in the relationship between sliding and extension at 0.7% is small compared with the change in the rate of creep: the rate of extension during the first 0.7% elongation (up to point 2 in

revealed sub-crystals in only a few grains. Those seen were relatively large; presumably the average size of the sub-crystals that would form was larger than the grain-size.

In Table II are given the sub-crystal diameter  $d$  and the quantity (grain-boundary sliding)  $\div (E_{\text{total}}^{\circ} - E_{\text{og.b.}}^{\circ})$ , where  $E_{\text{total}}^{\circ}$  is the measured elongation; this quantity has the dimensions of length and in pure aluminium tested at 200° C. has been found to be very nearly equal to the sub-crystal diameter.<sup>1</sup> Table II shows that the equality was found only with aluminium tested at 350° C. or below; it is therefore not a general creep relationship.

On the aluminium sections the misorientation between sub-crystals could be measured, and from this the extension  $E_{\text{oslip}}^{\circ}$  due to grain deformation was calculated. Adding this to  $E_{\text{og.b.}}^{\circ}$  gave a total value in fair agreement with the measured elongation. For example, for one specimen tested at 400° C.,  $E_{\text{oslip}}^{\circ}$  was 13.6% and  $E_{\text{og.b.}}^{\circ}$  5.5%, giving a total of 19.1% compared with the measured elongation of 22.1%. The discrepancies were

such that if they were attributable entirely to errors in  $E\%_{\text{g.b.}}$ , this value would have to be doubled in extreme cases, meaning that the interior  $E\%_{\text{g.b.}}$  would be twice that calculated from surface measurements; while if they were ascribed to errors in  $E\%_{\text{slip}}$  this value would have to be increased by about one-fifth. Previous experience shows that the estimates of  $E\%_{\text{slip}}$  are usually below the actual values, so that in all probability there is a similar amount of sliding at grain boundaries at the surface and in the interior. In this way the measurements of misorientation help to show that the sliding which can be seen on the surface is of a similar magnitude to the sliding that takes place in the interior.

#### IV.—CONCLUSIONS

(1) Grain-boundary sliding was found to be approximately proportional to elongation in all tests. The only certain deviation from proportionality occurred in the case of copper and even then the change in the factor of proportionality was 300 times smaller than the change in the rate of elongation that occurred at the same time.

(2) A relationship found previously with aluminium, namely that sub-crystal diameter =

$$\frac{\text{grain-boundary sliding}}{E\%_{\text{total}} - E\%_{\text{g.b.}}},$$

is not generally true. This relation could be explained if the rate of creep were controlled by grain-boundary sliding,<sup>1</sup> but as this seems not to be so (see "Discussion") the previous validity of the relationship was probably accidental.

#### V.—DISCUSSION: MECHANISM OF GRAIN-BOUNDARY SLIDING

The persistence throughout each creep test of a virtually constant proportionality between sliding and elongation suggests that grain-boundary sliding and crystallographic slip, as the only two significant deformation mechanisms at these temperatures, are controlled by the same process. Dorn's observation<sup>5</sup> that the rates of sliding\* and extension in aluminium have the same temperature coefficient when the stress is kept constant, and Martin, Herman, and Brown's similar observation<sup>6</sup> for brass, also afford very strong evidence for this conclusion. A plausible deduction from their work is that at constant stress the activation energy is the same for slip and sliding.

The simplest concept is that sliding controls slip or vice versa. As long as the evidence available gave the sub-crystal diameter equal to the quantity (grain-boundary sliding)/( $E\%_{\text{total}} - E\%_{\text{g.b.}}$ ), it was tempting to argue that sliding was the controlling process, since the equality could then be explained. But as, according to the present work, this relationship is not general, the argument loses force. No other clear evidence is known which suggests that sliding controls slip.

On the other hand, evidence exists in the case of two alloys that slip controls sliding, for in these particular metals the creep rate is suddenly reduced at a certain stage in the test, apparently by a structural change in the grain interior, and the rate of grain-boundary sliding follows suit. One is the copper-beryllium alloy, which in the present work showed a second deceleration in creep rate after 20 hr., which seems explicable only by some process in the interior of the grain, such as strain-ageing. Cottrell<sup>7</sup> has suggested that a similar effect in zinc<sup>8</sup> is due to strain-ageing, and this is a likely explanation here, since, according to the equilibrium diagram,<sup>9,10</sup> the copper-beryllium alloy was saturated with beryllium at the temperature of the test and the beryllium atom differs considerably in size from the copper atom. The alloy did, in fact, harden from 50 to 60 V.H.N. in the course of the test. The other alloy is  $\beta$ -brass, in which the rate of elongation and the rate of sliding are both abruptly reduced severalfold when the test temperature is lowered below the temperature at which the lattice becomes ordered.<sup>6</sup> Since the experimental relationship between slip and sliding is similar in all the materials tested, in the absence of evidence to the contrary the simplest idea is that the interaction between slip and sliding is similar in all metals. For slip to control sliding would then be the general rule.

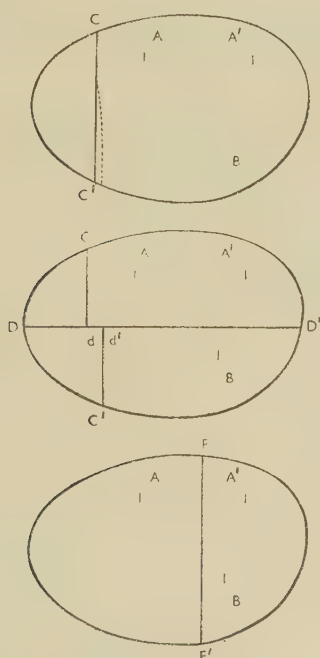
A model which can make slip the chief controlling process is that in which sliding occurs at first at the rate permitted by the grain-boundary "viscosity", but is increasingly impeded by irregularities along the boundary and eventually can proceed only if these irregularities are sheared through. This model is a little ambiguous, since it is not certain at what point in practice control by viscosity gives way to control by the resistance to grain deformation in the irregularities. It certainly puts very short-distance sliding (presumably sliding over too short a distance to be measured in the present work) under the control of viscosity and very long-range sliding under the control of slip, which contradicts the evidence mentioned later that both are controlled by the same process. More conclusively, the shearing of the irregularities would have to proceed under a high stress concentration in order to produce the intense shear in a thin layer that is observed; this means that when shear is the controlling process sliding and grain deformation proceed by creep under markedly different conditions, and a linear relationship between the two during the course of creep, and perhaps also equality of activation energy, are not to be expected. Consequently this model does not seem feasible.

A process by which the slip movements that control sliding take place under conditions virtually identical with those governing general grain deformation is illustrated by Fig. 13, showing an area of grain boundary (one grain lies above the plane of the paper and the other below) which contains three short ledges  $A$ ,  $A'$ , and  $B$ . The first result of applying a stress is to produce a small displacement of the upper crystal over the lower one, e.g. such that the full line  $CC'$  moves to the dashed position. If all the ledges held, nothing more would happen until a suitable plastic shear occurred in one of the crystals and redistributed the stresses. Thus, suppose that a screw dislocation  $DD'$  (Fig. 14) eventually reaches the boundary

\* For brevity, "sliding" is used to describe grain-boundary sliding and "slip" is used to denote crystallographic slip.



between *A* and *B*, producing the shear  $dd'$  and increasing the stress on ledge *B*. This process occurring repeatedly in many places will eventually overload a weak ledge, which yields, and an avalanche of sliding ultimately ensues. When a ledge yields, a dislocation loop will be despatched into each crystal, the two ends of the loop necessarily joining the boundary at the points where the ends of the former ledge were. If the ledges, and therefore the loops, are small, the line tension in the loops will make them contract when the stress concentration which caused them has been relaxed by sliding, and the ledge will be re-formed. Statistically, the grain-boundary geometry is then not altered by sliding. On the average, a given amount of slip continues to be associated with a given amount of sliding. Consequently, slip and sliding on average vary in unison, although locally sliding is jerky, as experiment confirms.<sup>11,12</sup>



FIGS. 13-15.—Illustrating Slip Movements at an Area of Grain Boundary.

The real situation is probably more complicated than this, because slip movements similar to that depicted in Fig. 14 can be imagined which impede sliding. For example, suppose a screw dislocation in one grain ends on the boundary, lies normal, and moves parallel to the boundary along  $FF'$  (Fig. 15). It will leave in its wake a ledge  $FF'$  (Fig. 15), which, if of the right sign, will oppose sliding. A dislocation is also formed in the other grain at the same time. If this process occurred uniformly during creep, it would steadily reduce the amount of sliding compared with the amount of grain deformation. Arguing from the experimentally observed constant proportionality between sliding and elongation, it may be supposed that this process takes place only at the very beginning of creep.

If slip is to control sliding, the grain boundaries must be relatively fluid even at low temperature (e.g. 100° C.

for aluminium in the present work), as otherwise their "viscosity" would restrain sliding and the rate of sliding would need to bear no relationship to the rate of grain deformation. The current idea that the viscosity of grain boundaries increases very rapidly with fall in temperature is, of course, not supported by any direct experiment, but is based chiefly on analogy with glass, the grain boundary being regarded as a layer of supercooled liquid. But glass possesses a complex structure and has, for example, a much higher temperature coefficient of viscosity than that of liquid metals. A better analogy exists with liquid metals, which have relatively small temperature coefficients of viscosity and would allow very much faster sliding than is observed. For example, extrapolating from the liquid region, under a shear stress of  $4 \times 10^7$  dynes/cm.<sup>2</sup> ( $\frac{1}{4}$  ton/in.<sup>2</sup>) and at a temperature of 200° C., a supercooled liquid layer of aluminium 10 Å. thick would shear at the rate of 0.23 cm./sec. (the viscosity of liquid aluminium is 0.0017 exp. (5500/RT)<sup>13</sup>), compared with the measured rate<sup>1</sup> of grain-boundary sliding of  $5 \times 10^{-8}$  cm./sec. This large difference is typical of other metals and allows for a considerable error in treating a grain boundary as a thin layer of supercooled liquid.

It appears that sliding should, nevertheless, be inhibited at low temperatures by the fact that the stress then necessary to produce plastic deformation causes slip bands to impinge on the boundary—sometimes slip bands in both grains impinge on the same point—producing ledges that are large on the atomic scale and which must impede sliding (Fig. 15). In addition, the number of active slip sources increases sharply as the stress increases, and the proportion that assists boundary sliding probably decreases. This kind of effect may be responsible for some of the variation with stress of the ratio sliding : elongation and for the plateaux in Fig. 10.

According to this model, small-scale sliding, such as is thought to occur in torsion pendulum tests, should also be controlled by slip. Some evidence that small- and large-scale sliding are controlled by the same process is provided by the fact that the activation energies for both are the same within experimental error, as shown in Table III :

TABLE III.—Activation Energies (cal./mole) Determined in Torsion Pendulum Tests and in Large-Scale Sliding.

Metal	Aluminium	Ref.	Tin	Ref.	Copper	Ref.
Torsion pendulum test	34,000	14	19,000	15	33,000	16
Direct test	37,000	5	19,200	12	31,000	17

Moreover, the energy dissipated at grain boundaries (applied shear stress  $\times$  mean distance of sliding), in the present tests on aluminium, when plotted against test temperature shows a peak at 210° C. comparable with the internal-friction peak in a torsion pendulum test; this is illustrated in Fig. 16. Included in this figure is a curve due to Kê,<sup>18</sup> the peak for which occurs at 280°–290° C., the strain rate being  $10^{-4}$ /sec., i.e. 180 times faster than in the present experiments. Using Kê's value for the activation energy, his peak would occur at 190°–200° C. for the latter rate of sliding, so that on this point

also there is fair quantitative agreement between the behaviour in small- and large-scale sliding.

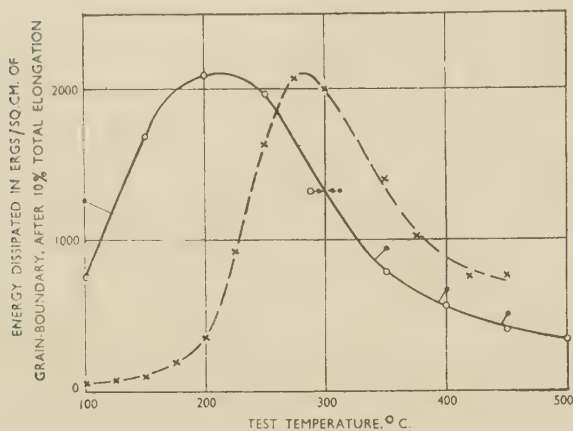


FIG. 16.—Energy Dissipated by Sliding at Grain Boundaries in Aluminium.

KEY  
 ○ Tapered specimens.  
 ● Parallel-sided specimens  
 — × — Ké's results.<sup>18</sup> (The ordinate scale gives relative values only for this curve.)

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# THE NATURE OF MECHANICALLY POLISHED METAL SURFACES: THE SURFACE DEFORMATION PRODUCED BY THE ABRASION AND POLISHING OF 70 : 30 BRASS \*

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## SYNOPSIS

The structure and depth of the deformed layer produced on surfaces of polycrystalline 70 : 30 brass by metallographic abrasion and polishing operations have been investigated systematically by a metallographic taper-sectioning technique. Based on this information, certain principles have been established for methods by which surfaces free from serious strains may be produced by mechanical methods of polishing.

Information has also been obtained relative to the theory of polishing. The similarity in structure of the deformed layers on abraded and polished surfaces suggests that fine metallographic polishing operations occur essentially by a cutting mechanism. This is in contradiction to the theory due to Beilby that polishing takes place by a process of surface flow. The metallographic evidence supporting the Beilby theory is critically reviewed, and it is concluded that it is now considerably less convincing than the evidence supporting the new theory. In particular, it is shown that the phenomenon of the apparent reappearance of scratches during the etching of polished surfaces can be explained more simply and more completely by the new theory.

## I.—INTRODUCTION

It is generally supposed that two fundamentally different layers are present in the surface of a metal specimen which has been polished mechanically. The outermost layer, which can be only some tens of Ångström units in thickness, is known as the "Beilby layer", and it is thought by many to be either amorphous or microcrystalline in nature;<sup>1-4</sup> however, some workers doubt the existence of the layer.<sup>5, 6</sup> In any event, it is generally agreed that beneath this layer there extends a zone which differs from the base metal only in having been deformed. The purpose of the present investigation was to study the nature and extent of the deformed layers produced by various metallographic abrasion and polishing operations, and to determine the principles of methods of polishing by which surfaces can be prepared with the minimum of deformation.

An arbitrary distinction will be made between the abrasion and polishing stages of preparation. Abrasion operations are defined as those in which the abrasive particles are firmly fixed during cutting; typical examples are abrasive papers and fixed-abrasive laps. Polishing operations are defined as those which are intended to produce a specularly reflecting surface in which the scratches are so fine that they are not readily detectable by optical methods of microscopy (although they can usually be detected by a sufficiently sensitive method of examination<sup>7</sup>). In metallographic practice, to which the present work is confined, this is accomplished as a rule by rubbing the specimen at a comparatively low pressure on a soft cloth pad charged with a suspension of a fine abrasive.

The technique employed by most earlier workers in this

field has been to remove successive layers of known thickness until the surface is found to be free from deformation; electron-diffraction,<sup>8-10</sup> X-ray-diffraction,<sup>11-14</sup> and metallographic methods<sup>15-18</sup> have all been used as tests for freedom from surface deformation. It seems, however, that metallographic taper-sectioning methods of the type adopted by Jacquet<sup>18</sup> offer considerable advantages, provided that a material is available in which deformation can be detected with high sensitivity by metallographic methods. Preliminary work<sup>19, 20</sup> has indicated that 70 : 30 brass meets this requirement well, and the taper-sectioning method was therefore adopted as the primary investigational technique.

## II.—EXPERIMENTAL METHODS

### 1. MATERIAL

The material studied was the cold-drawn polycrystalline  $\alpha$ -brass bar containing 29.6% zinc that was used in the preliminary investigations.<sup>19, 20</sup> The bar was cut into discs which were packed in alumina in a sealed steel tube and annealed. To facilitate metallographic examination, the annealing conditions for the specimens used for investigating abraded surfaces were chosen to give a coarse grain-size of approximately 0.4 mm. mean dia.; in studying polished surfaces the material was annealed to a finer grain-size of about 0.06 mm. mean dia. The hardness of the brass in both conditions was 45 D.P.N. After heavy pickling, the discs were mounted by casting in a cold-setting polyester resin. Mounting was necessary to enable accurate taper sectioning, but normal hot mounting was not feasible because of the copious deformation indications so introduced.<sup>19</sup>

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## 2. PREPARATION OF SPECIMENS

The method of preparation of the specimens is summarized below:

(a) A flat test surface was prepared by abrading the mounted specimen on a series of silicon carbide abrasive papers. The deformed layer was then removed completely by polishing on a wheel charged with a diamond-impregnated paste, the polishing time being determined by experience acquired during the investigation. Complete removal of the deformation could be confirmed by the fact that no indications of artefact were developed after etching by the most sensitive method available.

(b) The test surface was abraded as described in Section II, 3, or polished as described in Section II, 4.

(c) The test surface was heavily copper plated, first with a thin fine-grained deposit from a cyanide bath, the purpose of which was to increase the contrast at the section line, and then with a heavy deposit from an acid bath. The plated specimen was taper sectioned at a nominal taper ratio of 10:1 by a method, described elsewhere,<sup>21</sup> which enables the taper ratio of the finish-polished surface to be determined with accuracy. The section line was so arranged as to be as closely as possible perpendicular to the direction of the surface scratches; this factor is not of great importance, however, provided that all depth measurements on the section are made perpendicular to the section line.

(d) The taper-section surface was prepared for metallographic examination by methods which ensured removal of all the surface deformation produced during sectioning, the process being continued until the finish-polished surface was satisfactorily free from artefact indications when etched by the required method. The preliminary polishing was carried out by mechanical methods; the routine specimens were finish-polished by electrolytic methods,<sup>22</sup> but most of the sections used for the accompanying illustrations were finished mechanically by "skidding" on a paste of magnesium oxide.<sup>7</sup>

However, even with the most thorough methods of preparation, minor artefacts were sometimes developed by the most sensitive etching methods (the small indications at the extreme left of Fig. 3, Plate IX, are examples). It would appear that these indications result from very small strains introduced during handling. An advantage of the taper-section method is that it is possible to distinguish these artefacts from the true surface-deformation indications with reasonable certainty; even so, only minor artefacts can be tolerated (see Section III, 1). In the alternative metallographic method of removing successive layers from the surface, these artefacts could lead to over-estimation of the depth of deformation, which may account for the discrepancy in the results obtained by Jacquet<sup>18</sup> by the two methods.

(e) The polished taper sections were etched by one of the methods listed in Table I, selected from the results of the preliminary investigation.<sup>19</sup> The estimated maximum sensitivity of each etching method is also shown in this table. The characteristics of these etching methods were determined on specimens uniformly compressed by hammering or rolling, so that the sensitivity values quoted do not necessarily apply rigidly to the more complicated deformation process under investigation. However, these considerations affect only the absolute value of the strain level ascribed to the

base of the layer etched by a particular method, and this is not of great significance for the present purposes.

(f) The depth of the layer in which deformation indications were revealed by etching was measured on a

TABLE I.—*Etching Methods Selected for Investigating the Deformed Layers.*

Etching Method	Maximum Sensitivity in Detecting Deformation, % compression
Ferric chloride-hydrochloric acid reagent	2
Cupric ammonium chloride reagent	0.5
Electrolytic thiosulphate etch:	
Low-sensitivity method (0.5% solution at 1 amp./dm. <sup>2</sup> )	0.2
High-sensitivity method (0.25% solution at 3.5 amp./dm. <sup>2</sup> )	<0.05

metallurgical microscope, having a calibrated filar eyepiece. From a knowledge of the taper ratio of the section, the true depths could then be calculated.

## 3. ABRASION OF TEST SURFACES

The abrasion processes investigated were those using silicon carbide papers, emery papers, and a fixed-abrasive lap, since it is on one or other of these that the majority of methods of metallographic preparation are based. The silicon carbide papers were lubricated with a stream of water and the emery papers with kerosene; the abrasive lap was unlubricated. The study was confined to hand abrasion by the normal method representative of the best metallographic practice, which produces unidirectional scratches. Several attempts were made to develop a mechanical device with which a constant pressure could be applied to the specimen during abrasion, but all were unsuccessful, as they resulted in rather severe "rocking" of the specimen. Subsequent events showed that the abrasion pressure was not an important variable. The method of preparation was as follows:

The abrasive paper was clamped flat on a plate-glass backing by means of a sheet of stainless steel in which a window (1 × 10 in.) had been cut so as to expose a track to which the abrasion was confined. The track was worn with a dummy specimen of 70:30 brass before the abrasion of each test specimen, this latter being abraded for the last 20 strokes of each wear period. Specimens were prepared which were representative of successive wear periods of 20, 40, 80, 160, 320, 640, and 1280 abrasion strokes, these arbitrarily defined wear periods being referred to as Nos. 1-7, respectively. All abrasion was carried out by one operator, using a "normal" applied pressure of about 500 g./cm.<sup>2</sup>, but additional specimens were sometimes prepared by using a "light" abrasion pressure of about 100 g./cm.<sup>2</sup>. The specimens were abraded at a rate of about one stroke per second.

## 4. POLISHING OF TEST SURFACES

Only one polishing process was investigated, namely, hand polishing on a synthetic suede cloth charged with a (0-1)  $\mu$ -grade diamond abrasive, a unidirectional system of scratches being established at the end of the treatment. This process may be taken as a representative fine-polishing process. Particular care was taken in the preliminary preparation of the test surfaces for these



experiments, so that it was possible to be certain that the effects observed in the taper sections were attributable only to the polishing process.

## 5. MEASUREMENT OF ABRASION AND POLISHING RATES

The most satisfactory general method of determining abrasion rates is that due to McKee,<sup>23</sup> in which the thickness of the layer removed in a known time is determined from the change in dimensions of a diamond-pyramid hardness impression. This method, however, is unsuited to many polishing methods in which excessive rounding of the edges of the impression occurs. The polishing rates were therefore determined from the loss in weight of unmounted specimens.

## III.—METALLOGRAPHIC STRUCTURE OF THE DEFORMED LAYERS

### 1. ABRADED SURFACES

Examination of the sections after etching in the various reagents listed in Table I showed that the deformed layer on the abraded surfaces could be divided into the three zones discussed below.

#### (a) The Surface Zone of Severest Deformation

A dark-etching zone, the structure of which could not be resolved under the metallurgical microscope, was present at the surface (Fig. 5, Plate X, and Fig. 4, Plate IX). The zone was undulating in nature, contouring the abrasion scratches; its depth beyond the root of the scratches was usually 1–2 times the depth of the scratches themselves. The layer showed some gradation in etching contrast, but ended abruptly (Fig. 5, Plate X). The nature of this layer was not determined. It could be related to the dark-etching layer found by Moore and Tegart<sup>24</sup> beneath a track made by the repeated sliding of a rider on a copper surface, and thought by them to be a layer in which fine oxides had been occluded. It is difficult to see, however, how oxides could be occluded to depths of a micron or more during a single cutting traverse of an abrasive particle. It could simply be a shear zone, possibly affected to some extent by heating of the surface during cutting.<sup>25–29</sup>

#### (b) The Zone of Gross Deformation

In this zone, features which had all the characteristics of "slip-band indications" were developed; they were best shown by etching in the ferric chloride reagents (Figs. 1 and 4, Plate IX). These indications, which are thought to be associated with the formation of bands of lamellar slip,<sup>19</sup> extended in rays beneath individual abrasion scratches, the indications in each ray usually being slightly convex towards, and approximately parallel to, the surface (Fig. 4, Plate IX). This presumably indicates that heavy shear forces are developed parallel to the surface during cutting, as suggested by King and Tabor.<sup>30</sup> Some evidence of general distortion of the structure was also found in this zone; for example, distortion of the twin boundaries in line with the rays of deformation was sometimes noted (Fig. 6, Plate X).

#### (c) The Zone of Minor Deformation

Extending well beneath the zone of gross deformation was a zone in which "slip-line indications" could be developed (Figs. 2 and 3, Plate IX). The base of the layer of indications developed by the high-sensitivity electrolytic thiosulphate etch can, for all practical purposes, be taken as the elastic/plastic boundary;<sup>20</sup> the depth of this layer will be termed the "total depth of deformation". The zone did not show any noticeable tendency to be arranged in rays beneath the abrasion scratches, but did vary markedly in depth in an irregular manner across the sections. It is of some significance to note that these local irregularities could not be distinguished unless the section examined was almost completely free from artefact indications. Some evidence of deformation in the form of diffuse coloured bands extending in rays in line with the rays of slip-band indications was also developed in this zone by etching in the less-sensitive reagents (Fig. 4, Plate IX). They are presumed to etch by a special effect due to the presence,

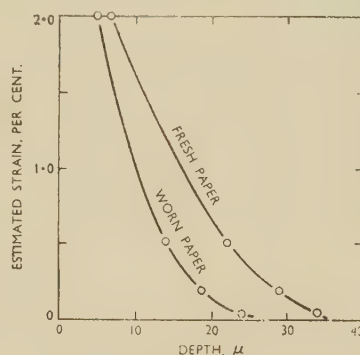


FIG. 27.—Estimated Strain Gradient in Abraded Surfaces. Surfaces abraded on a 600-grade silicon carbide paper at normal pressure.

immediately adjoining one another, of areas differing in orientation and strain.

With the exception of the high-sensitivity electrolytic thiosulphate etch, the features described above were developed most prominently in the lighter-etching grains. This is a feature of the mechanism of etching,<sup>19</sup> and there is no reason to doubt that the initiating deformation effects occur in all grains. These remarks apply also to the features observed in the polished surfaces discussed later.

If approximate strain levels, such as the values listed in Table I, are ascribed to the base of the layer of indications developed by each etching method, an estimate can be made of the strain gradient in the deformed layer; typical results are given in Fig. 27. The significant feature is that the strain gradient is very steep at the surface, but becomes shallow as the undeformed matrix is approached. Hence, the depth of deformation measured in a particular investigation would depend largely upon the sensitivity of the method used to detect deformation, a value which is not known for the methods used by most of the earlier investigators.<sup>8–18</sup>

## 2. POLISHED SURFACES

A deformed layer very similar in structure to that found on the abraded surfaces was detected on the polished surface. A confused dark-etching zone similar

to the surface zone of severest deformation could be distinguished after etching in the ferric chloride reagent (cf. Figs. 5 and 7, Plate X). Etching in the more-sensitive reagents developed slip-line indications, as in the zone referred to above as the zone of minor deformation (cf. Fig. 9, Plate X, and Fig. 2, Plate IX; Fig. 11, Plate X, and Fig. 3, Plate IX). In this case, the slip-line indications were aligned in rays beneath the polishing scratches, and the strains in the layer, as judged by the intensity of the slip-line indications, were of a much lower order of magnitude than in the layer on abraded surfaces. In fact, the slip-line indications developed by the high-sensitivity electrolytic thiosulphate etch were of a very degenerate form and were only just recognizable as such (Fig. 11, Plate X). The zone of gross deformation containing slip-band indications was not observed on the polished surface.

The similarity between the metallographic structures of the abraded and polished surfaces strongly suggests that the principal mechanism operating is the same in the two cases. This means, in effect, that the polishing process investigated occurs essentially by a cutting mechanism. The two processes, however, differ considerably in degree, as evidenced by the less-marked nature of the slip-line indications in the zone of minor deformation and the absence of the zone containing slip-band indications; the latter indicates that the shear strain in the immediate sub-surface layers does not exceed the threshold value necessary for the initiation of lamellar slip.<sup>19</sup>

#### IV.—THE DEPTH OF THE DEFORMED LAYERS

The following measurements were made on the taper sections:

(i) The depth of scratches ( $D_s$ ): defined as the maximum roughness, from crest to root, of local groups of scratches.

(ii) The depth of gross deformation ( $D_G$ ): defined as the maximum depth beneath the root of the scratches of the layer of gross deformation.

(iii) The total depth of deformation ( $D_T$ ): defined as the maximum depth beneath the root of the scratches of the layer of minor deformation developed by the high-sensitivity electrolytic thiosulphate etch. It was necessary to record two values for  $D_T$ , namely, the depth of the local maxima in the layer (the "maximum depth") and a depth more generally representative of the surface (the "average depth").

##### 1. SURFACES ABRADED ON SILICON CARBIDE PAPERS

###### (a) Effect of Wear of the Abrasive Paper

In the early stages of wear, the expected effect was observed in that  $D_s$ ,  $D_G$ , and  $D_T$  all progressively decreased as the paper became worn,  $D_T$  in particular decreasing markedly (Fig. 28). However, the papers soon reached stability, all the above values thereafter remaining substantially constant over the full wear range investigated. Stability was reached earlier with finer grades of paper. These results imply that, contrary to the usual recommendations, there is no real advantage in using very well-worn paper.

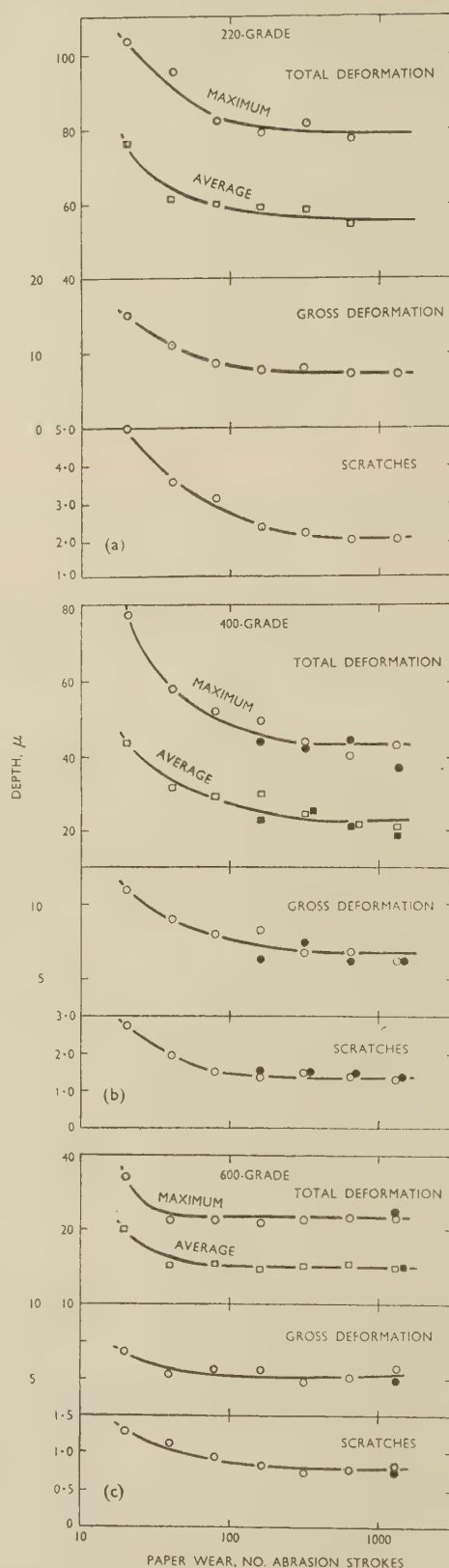


FIG. 28.—Variation of Depth of Scratches and Associated Deformation with Increasing Wear of Silicon Carbide Papers.

Open points: normal abrasion pressure.  
Closed points: light abrasion pressure.



There was a noticeable change in the distribution of the deformation during the early stages of the wear of the papers. The rays of slip-band indications in specimens which had been abraded on fresh paper were relatively widely spaced, and were narrow and deep; when stability was reached, the rays of indications were much more numerous and uniform, and were broader; thereafter, the form and distribution of the rays remained substantially unchanged. The abrasion scratches followed a similar course. It would appear that, when the paper is fresh, the specimen is abraded mainly by a relatively few abrasive particles with sharp points which stand above the general level; these produce deep sharp scratches and deformation zones. If these particles are torn out of the abrasive paper or if their points wear, larger numbers of particles of a more uniform rounded shape will then contact the surface, producing the broader more uniform rays of deformation.

### (b) Effect of Abrasion Pressure

In every instance where a comparison was made between specimens prepared with "normal" and "light" abrasion pressures, no significant difference was found in the measured values of  $D_S$ ,  $D_T$ , and  $D_G$  (Fig. 28 (b) and (c)). There was, however, a difference in the distribution of the scratches and associated rays of deformation. The maximum depth values recorded in Fig. 28 were attained fairly uniformly across specimens abraded at high pressures. At light pressures, on the other hand, the values varied much more widely, the maximum values being obtained only at infrequent localized areas. Nevertheless, a surface must be judged on the maximum depth of deformation, and these results clearly establish that there is no real advantage in using light pressure during abrasion, as is so commonly recommended.

An approximate static model to explain this result can be devised, as follows: Contact between the specimen and abrasive paper is at first made by only a few abrasive particles whose cutting points stand above the general level. When a load is applied to the specimen, the load carried by each of these particles increases and they indent the specimen surface, the mean pressure over the area of contact of each particle remaining constant and proportional to the yield point of the material (Tabor<sup>31</sup>). The paper-and-glue support to the particles, however, is not completely rigid, and it may be expected that each particle can sustain only a certain limited load. When this load is exceeded, indentation of the specimen ceases,\* and the particle sinks into the support until adjoining particles come into contact with the specimen surface, so supporting the additional load. Each particle that comes successively into contact with the surface may be expected to go through a similar cycle. The end result is that the external load determines only the number of abrasive particles which reach the condition of maximum indentation.

This mechanism implies that the maximum depth of indentation, and hence the depths of scratches and associated deformation, will be smaller the less rigid is the support to the abrasive particles; a further reduction may be expected when the particles are not fixed, but

can roll at a certain stage. Effects of this type offer a reasonable explanation of the considerable difference in degree between abrasion and polishing operations.

### (c) Grade of Abrasive Paper

The papers tested were 220-, 440-, and 600-grade, respectively, these constituting the most convenient series for metallographic purposes. The results for each grade are shown in Fig. 28 (a)–(c), the average values for stabilized paper being summarized in Table II. The

TABLE II.—Summary of Measurements of Depths of Scratches and Associated Deformed Layers, and of the Abrasion Rates of Various Abrasion Processes.

Abrasion Stage		Depth, $\mu$				Abrasion Rate over Optimum Wear Range, $\mu$ /min.
		Scratches ( $D_S$ )	Gross Deformation ( $D_G$ )	Total Deformation ( $D_T$ )		
Type	Grade			Average	Maximum	
Silicon carbide papers	220	2.0	7.5	55	77	45-90
	400	1.5	6.5	23	43	25-60
	600	0.75	5.0	15	22	15-40
Emery papers	1/0	1.8	7.5	30	45	20-35
	2/0	1.0	7.0	24	38	20-35
	3/0	0.4	4.0	18	30	10-17
	4/0	0.3-1.0 *	3.0-10 *	15	20-50 *	5
Alumina-wax lap	(10-20) $\mu$	0.3	3	8	16	...

\* Depending upon the condition of the paper.

results indicate that these papers form a satisfactory series in that the maximum scratch depth and total depth of deformation decreases in proportion.

## 2. SURFACES ABRADED ON EMERY PAPERS

The emery papers showed the same general characteristics as the silicon carbide papers, the results for stabilized paper being summarized in Table II. It will be noted that, although the depth of the abrasion scratches decreased proportionately with increasing fineness in the grade of paper, the depth of deformation did not. As a result, the depth of deformation with the finer grades was greater than for the equivalent grades of silicon carbide paper, even though the scratch depth was less. It is on the depth of deformation, rather than on the depth of scratches, that the papers must be judged. The results for the 1/0- and 2/0-grade papers were in reasonable agreement with those obtained by Jacquet by a similar experimental method.<sup>18</sup> However, Jacquet appears to have overlooked the local maxima in the total depth of deformation; this might have been due to the presence of excessive numbers of artefact indications in his sections (see Section III, 1).

The 4/0-grade paper was an exception to this general pattern of behaviour. After the paper had been used for a short while, all the measured values increased markedly and then varied erratically from specimen to specimen over the range indicated in Table II. This

\* Alternatively, the cutting points may crush; there is, however, little evidence that this occurs with metallographic abrasion papers.

was due to the appearance of occasional very rough gouged areas in the surface with associated deep rays of deformation. It is thought that these result from clogging of the paper with abrasion debris, packed areas of debris causing metal to be plucked out from the surface (Bowden and Tabor<sup>32</sup>).

A very similar phenomenon was found to occur with all grades of emery paper when used unlubricated. On the other hand, when a liquid lubricant was used, its nature had no detectable effect on the results; for example, the incorporation of wax in solution in the kerosene did not reduce the depth of either the abrasion scratches or the surface deformation. This suggests that the essential function of a lubricant is to prevent the paper from clogging with debris and that, if this is achieved, one lubricant is as effective as another. In this event, it does not act as a "lubricant" in the usually accepted sense. This is in conformity with the ideas of Bowden and his co-workers,<sup>32</sup> who maintain that a high temperature is reached at the cutting point of an abrasive particle, the maximum temperature being uninfluenced by the surrounding liquid; ordinary liquid lubricants could not be expected to function as such at these temperatures.

### 3. SURFACES ABRADED ON A FIXED ABRASIVE LAP

The lap investigated was a cast abrasive-wax type prepared with a (10–20) $\mu$ -grade of alumina;<sup>7</sup> it can be taken as representative of the best practice with fixed-abrasive laps. The results obtained with a specimen abraded at normal pressure on a fresh lap are given in Table II. These laps clog with debris when used either dry or lubricated; the depth of deformation produced on a clogged lap was about double that shown in Table II. The laps were, however, less critical in this respect than 4/0-grade emery paper. Serious clogging did not occur until after about 10 minutes' use, by which time the cutting efficiency of the lap has been seriously impaired (see Section V, 1).

### 4. POLISHED SURFACES

The maximum depth of the polishing scratches in the surface investigated was about 0.05  $\mu$ . The dark-etching surface layer of severest deformation was about 0.1  $\mu$  in depth over most of the surface, although more marked rays of the type shown in Fig. 7 (Plate X) extended to depths of up to 0.7  $\mu$ . The maximum depth of the layer of minor deformation was about 4  $\mu$ .

## V.—CONDITIONS FOR THE PREPARATION OF SURFACES FREE FROM DEFORMATION

It was apparent by this time that any major deformation found in a finish-polished surface almost certainly originated during the preliminary abrasion of the surface. One of the most important ultimate aims of a process of preparation must be to free the surface from as much of this deformation as possible. Ignoring for the present any deformation produced during original cutting or machining of the surface, means of meeting this requirement are best considered in two stages: first, the removal of the pre-existing deformed layer at each successive

abrasion stage, and, secondly, the removal during polishing of the deformed layer remaining at the end of the abrasion stage of preparation.

### 1. REMOVAL OF THE DEFORMED LAYER DURING SUCCESSIVE ABRASION STAGES

Estimates were made of the abrasion rates of the abrasive papers under consideration at approximately the same wear periods as previously. The abrasion was carried out at normal pressure by the methods described in Section II, 3, and the results are expressed as  $\mu$ /min. The reproducibility of the results was quite good, and those obtained by independent operators were similar (Fig. 29). They may be taken as a reasonable indication of the abrasion rates likely to be attained in practice.

In general, the abrasion rates decreased in an exponential manner with wear of the paper, the results for the silicon carbide papers being shown in Fig. 29. It

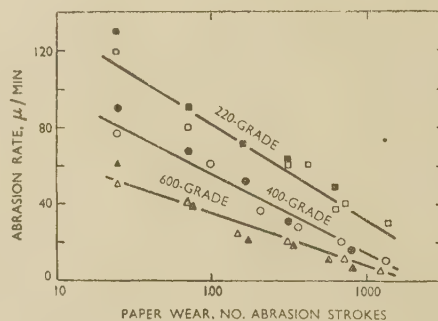


FIG. 29.—Variation in Abrasion Rate with Increasing Wear of Silicon Carbide Papers. Abrasion at normal pressure; 220-, 400-, and 600-grades.

Open points: operator A.  
Closed points: operator B.

follows that the papers are in an optimum condition for use over a range in the middle of their life; the depth of deformation is unnecessarily great if they are used when too new and the abrasion rate is reduced seriously if they are too old. The latter condition is usually reached before the paper shows obvious signs of deterioration.

The abrasion rates to be expected over the selected optimum wear range (wear periods 3–6, see p. 52) are summarized in Table II. Note that the abrasion rates of the silicon carbide papers are much higher than those of the comparable grades of emery paper. This is of particular interest in the case of the coarsest grades, since it indicates that it would be much more difficult to remove the effects of preliminary cutting and machining processes on the emery papers than on the silicon carbide papers. Note also that the abrasion rate of the 3/0-grade emery paper is only just comparable with, and that of the 4/0-grade considerably less than, the polishing rates of rough-polishing processes (cf. Table III).

From the data given in Table II, it is easy to see that abrasion times of the order of 5 min. would be necessary to remove completely the pre-existing deformation at each successive stage on either series of papers. However, an abrasion time of only 0.5 min. would be necessary with comparatively new paper to reduce the depth of



the pre-existing layer to the depth of that being produced by the next stage; this is all that is required in practice. The corresponding time for paper worn to the end of its optimum life period is about 2 min.; this is becoming too long for convenience, which emphasizes the desirability of using new paper. Moreover, it is to be expected (and a few tests have confirmed) that the abrasion rate would be inversely proportional to the abrasion pressure. It is obviously preferable, therefore, that the abrasion pressure should be as high as possible, remembering that this will have no serious effect on the depth of the deformed layer being produced. Even under the best conditions, however, a treatment of substantial duration is required on each abrasive paper; the classical recommendation that abrasion be carried out for as long again as it takes to remove the pre-existing scratches is clearly quite inadequate.

Abrasion-rate tests were also carried out on the abrasive-wax lap. The useful cutting life of the lap is about 1.5 min., in which time a total thickness of about 25  $\mu$  is removed. It should be practicable to reduce the deformed layer produced on a 400-grade silicon carbide paper to that being produced on the lap. The lap may therefore be substituted with advantage for the 600-grade of silicon carbide paper.

Summarizing, it is possible to abrade a specimen through either of the abrasion series under consideration so that the depth of the deformed layer finally is that listed in Table II for the final stage of the series. For this to be so, however, certain precautions must be taken during abrasion.

## 2. REMOVAL OF THE ABRASION DEFORMATION DURING POLISHING

The polishing rates of unmounted specimens of 70 : 30 brass were determined on polishing pads charged with the abrasives listed in Table III. The tests were carried out on a mechanical wheel (300 r.p.m.) covered with a napped cloth, the specimen being rotated by hand in a direction contrary to that of the wheel at an applied pressure estimated to be about 200 g./cm.<sup>2</sup>. The polishing pads have been grouped into: (a) rough-polishing processes representative of those used in some polishing methods<sup>33-36, 7</sup> specifically with a view to eliminating the damage produced during abrasion, and (b) fine-polishing processes representative of those intended to produce a final polish. Many classical methods<sup>37-39</sup> confine polishing operations to processes of the latter type.

From these results, the time required to remove the deformation produced by abrasion under optimum conditions, namely, through the series 220-grade and 400-grade silicon carbide papers and (10-20) $\mu$ -grade cast alumina-wax lap, has been calculated (Table III). Two values are given, viz. the polishing time required for complete removal of the deformed layer, and the time required for its elimination to a residual surface strain level estimated at about 1% compression. It is considered that the latter might be adequate for many purposes. It is apparent that there can be little expectation in practice of achieving either of these results unless a stage with a high polishing rate is included in the polishing procedure. Since this entails the use of coarse abrasives, polishing generally must be carried out in two

stages, i.e. a first or rough-polishing stage intended essentially to remove the abrasion deformation, and a second fine-polishing stage (or series of stages) intended to produce a satisfactorily scratch-free surface. A few exceptions may be found to this generalization where it is possible to combine the two stages to some degree, e.g. by the use of proprietary metal polishes which result in very strong polish-attack in the case of copper alloys.

For comparison, the polishing time required to remove the abrasion deformation by a standard method of electrolytic polishing is also shown in Table III. Long

TABLE III.—Polishing Rates of Representative Polishing Methods, and Polishing Times Required for the Removal of Abrasion Deformation.

This table refers to abrasion on the series 220-grade, 400-grade silicon carbide papers, (10-20) $\mu$ -grade cast alumina-wax lap. The polishing times required after abrasion on the series 1/0-, 2/0-, 3/0-grade emery papers would be at least double those listed.

Polishing Method	Polishing Rate, $\mu$ /min.	Polishing Time for Removal of Abrasion Deformation, min.	
		Complete Removal	Residual Strain of 1% Compression
(a) Rough Polishing:			
Alumina, (10-30) $\mu$ .	7.5-10	2.0	0.9
Diamond, (4-8) $\mu$ .	15-17	1.0	0.5
(b) Fine Polishing:			
Alumina, (0-0.3) $\mu$ .	1.0-2.0	15	7
Rouge .	1.5-2.5	10	5
Magnesium oxide .	0.1	150	70
(c) Electrolytic Polishing *	0.6	25	11

\* Orthophosphoric acid bath (Jacquet<sup>22</sup>).

treatment times are practicable in this case, but it must be realized that electrolytic polishing treatments of inadequate duration would result in surfaces containing residual abrasion strain, in the same manner as ineffective polishing by mechanical methods.

## 3. SUMMARY OF PRINCIPLES OF METHODS FOR PRODUCING SURFACES FREE FROM ABRASION DEFORMATION

It is now possible to establish a number of principles for methods by which surfaces free from serious strains may be produced. These are summarized below:

(1) Silicon carbide papers are to be preferred to emery papers for the abrasion stages of preparation. Their advantages are: (a) the abrasion rates are appreciably higher, (b) they constitute a better-graded series, (c) the final depth of deformation is less, and (d) it is possible to use water as a lubricant, which is both efficient and convenient.

(2) The optimum conditions of use of abrasive papers are: (i) the paper should be in a slightly worn, but not excessively worn condition, (ii) the abrasion pressure should be as high as is convenient, and (iii) a liquid lubricant should be applied to prevent the paper clogging with abrasion debris.

(3) A treatment of substantial duration is required on each abrasive paper.

(4) A fixed-abrasive lap, if used in a fresh condition, is of some advantage as a final abrasion stage.

(5) It is possible to remove the abrasion deformation either entirely or to a reasonable residual strain level by mechanical methods of polishing. For this to be so, however, it is essential that abrasion shall be followed by a rough-polishing stage with a high cutting rate designed specifically to remove the abrasion deformation.

## VI.—THE INFLUENCE OF THE SURFACE DEFORMATION PRODUCED DURING POLISHING ON THE DEVELOPMENT OF SCRATCH TRACES

Even if the abrasion deformation is removed completely during polishing, the polished surface will normally contain rays of deformation of the type described in Section III, 2, extending beneath the polishing scratches. One important effect of these rays of deformation will be discussed in this section.

Surfaces of 70:30 brass polished on a (0-1) $\mu$ -grade diamond-abrasive pad contain numerous very fine polishing scratches which are scarcely visible under bright-field illumination, but which are readily detectable under phase-contrast illumination (Fig. 13, Plate XI). When a surface of this type was etched in a reagent having comparatively low sensitivity to deformation, such as the ferric chloride reagent, the scratches were rendered easily visible in bright-field illumination (Fig. 15, Plate XI); in addition, the colour contrast between the grains was poor (cf. Figs. 15 and 18, Plate XI). If a surface of this type was polished by skidding on a water paste of magnesium oxide, no evidence of the diamond-abrasive scratches was found even under phase-contrast illumination (Fig. 14, Plate XI). However, features appeared when the surface was etched in the ferric chloride reagent which seemed to be related to the diamond-abrasive scratches (Fig. 16, Plate XI); these features will be called "scratch traces" to distinguish them from definite scratches on the original polished surface. The number of scratch traces developed by etching decreased with increase in the skidding time.

Similar results were obtained when the surfaces were polished for a standard time-interval on pastes containing increasing amounts of ammonium persulphate in solution, the scratch traces developed by etching in the ferric chloride reagent disappearing completely with sufficiently high concentrations of persulphate (Figs. 17 and 18, Plate XI). However, if a surface which would have contained only faint scratch traces after etching in the ferric chloride reagent was etched instead by methods with higher sensitivity in detecting deformation, numerous scratch traces were developed, the number increasing with increase in the sensitivity of the etching method (cf. Figs. 17, 19, and 20, Plate XI).

When these scratch traces were examined at high magnifications, it was apparent that they were not grooves. The traces developed by the ferric chloride reagent consisted of differentially coloured bands in

light-etching grains and diffuse bands in the dark-etching grains (Fig. 8, Plate X). The traces developed by the more sensitive reagents were bands of slip-line indications\* (Figs. 10 and 12, Plate X). When these micrographs (Figs. 8, 10, and 12, Plate X) are compared with the micrographs of the taper sections of the surface polished on a (0-1) $\mu$ -grade diamond pad (Figs. 7, 9, and 11, Plate X), it is evident that the appearance of the scratch traces can be explained as follows:

The original (0-1) $\mu$ -grade diamond finish showed poor colour contrast on etching because of the presence of the dark-etching surface layer of severest deformation. It may be assumed that skidding on a magnesium oxide pad, with or without the addition of an etching reagent to the paste, removes material from the surfaces; the strong grain-relief developed during skidding (Fig. 14, Plate XI) supports this contention. It is possible, then, that the surface may be reduced beneath the root of the polishing scratches, but not beneath the root of the associated rays of deformation, leaving bands of locally deformed material in the surface at the sites of some of the pre-existing scratches. These bands are attacked preferentially during etching and appear as scratch traces. In the case of 70:30 brass, the traces are etched because of the unusual sensitivity of the etching methods to deformation. It may well be supposed, however, that, even in less favourable circumstances, differential etching of scratch traces could still occur owing to the close juxtaposition of deformed and undeformed material in the surface. In this event, it is probable that only the deformed layer equivalent to the surface zone of severest deformation would give rise to scratch traces.

Support for these assumptions was obtained in experiments with an optically anisotropic material, namely, zinc. A specimen of polycrystalline zinc was polished on the diamond abrasive pad as before and then finish polished by skidding on an aqueous paste of magnesium oxide for a short period (about 1 min.). It was then examined under bright-field, phase-contrast, and polarized-light conditions, and the same area was re-examined after etching in a standard chromic oxide/sodium sulphate reagent.

In the finish-polished condition, the usual undulations aligned in the direction of the diamond-abrasive scratches were visible under phase-contrast illumination (Fig. 21, Plate XII), but no scratches appeared to be present; scratches were not detected under bright-field illumination. Under polarized light, bands which differed in polarization contrast and which were aligned in the direction of the pre-existing diamond-abrasive scratches could be observed on the surface (Fig. 23, Plate XII); these bands reversed contrast in phase with the twins present in the parent grains during rotation of the specimen with respect to the plane of polarization (cf. Figs. 23 and 24, Plate XII). It seems clear that the bands are the remnants of rays of deformation associated with the diamond-abrasive scratches which, in this material, can be expected to be twin areas; examination at high magnifications even gave some evidence of a twin-like

\* A peculiar feature of the scratch traces shown in Fig. 12 (Plate X) was that the etching indications developed in a narrow line at each edge of the trace. The corresponding rays of

indications in the taper sections (Fig. 11, Plate X) were also in the form of a double band. The reason for this is not clear.



structure in the bands (Fig. 25, Plate XII). Scratch traces developed during etching at the sites of the more prominent of these bands (cf. Figs. 22 and 23, Plate XII), as predicted by the above theory. The same results were obtained when the final polish was carried out with fine alumina, although the finish was then lightly scratched and the effects were not so clearly shown.

The appearance of scratch traces on etching is a well-known phenomenon but the explanation accepted hitherto has been one based on the theory due to Beilby<sup>1</sup> that polishing occurs by a process of surface flow. Beilby supposed that "amorphous" material is flowed into the surface scratches during polishing and that this material, being unusually reactive, is preferentially attacked during etching, so re-exposing the scratches. However, this theory is quite incapable of explaining the detailed characteristics of the scratch traces described above. Moreover, the mechanism proposed here to account for these new observations provides a much simpler general explanation of the phenomenon.

## VII.—DISCUSSION

The investigation has established that deformation of the surface layers of a metal specimen occurs during both abrasion and polishing operations. However, ignoring for the moment the superficial layer referred to as the surface zone of severest deformation, the strains induced during polishing are of a much lower order of magnitude and extend for considerably shallower depths than those induced during abrasion.

Once the magnitude and extent of the strains produced during abrasion are recognized, it is apparent that a new approach is necessary to the design of surface-preparation procedures for metallographic purposes, based on considerations of the extent and removal of surface deformation rather than of surface scratches. The present experiments have established certain principles based on these considerations (summarized in Section V, 3) which, however, apply strictly only to specimens of annealed 70 : 30 brass. This material was chosen for investigation for reasons of experimental technique rather than because of its representative nature. The results are difficult to apply exactly to other materials, because the depth of deformation produced by a given process might be expected to be related approximately to the hardness of the specimen material, whereas polishing and abrasion rates appear to be more closely related to the melting point than to this property.<sup>40, 7</sup> Nevertheless, the general conclusions at least should be applicable to most common cubic materials of similar or lower melting point.

Perhaps the most important of the principles established is the need to incorporate in the polishing process a rough-polishing stage giving the maximum possible polishing rate; mechanical polishing methods of this type are available which should be capable of reducing the abrasion strains to a reasonable level in most common materials. Many classical mechanical polishing methods, however, do not incorporate such a rough-polishing stage, and it is to be expected that surfaces prepared by these methods might contain strains of a high magnitude remaining from the abrasion deformation. This is more likely to be the source of the surface deformation so

frequently reported as present in mechanically polished surfaces, than is deformation introduced during polishing itself. For example, residual abrasion deformation almost certainly accounts for the anomalously high hardness values obtained in low-load hardness tests,<sup>41-49</sup> for the recrystallized layers found after thermal etching<sup>50, 51</sup> or after annealing,<sup>52, 53</sup> for the development of "maze" magnetic colloid patterns,<sup>54-56</sup> and for the presence of deformation artefacts in mechanically polished surfaces.<sup>33, 57-62</sup> Criticisms of mechanical methods of polishing based on these considerations (e.g. Jacquet<sup>63-66</sup>) cannot therefore be regarded as general, but as applicable only to the particular method of polishing employed by the investigator concerned.

The seriousness of the surface strains introduced by a fine-polishing operation can be assessed only in individual cases, and for a particular end-use. The layer of minor deformation is likely to have serious consequences only in rare instances where the last vestiges of the abrasion deformation have to be removed. The surface layer of severest deformation, however, is more likely to have serious effects. For example, it may easily result in irregular etching of the surface, the exaggeration of scratches during etching, and the development of scratch traces. It may also be the layer responsible for the suppression of "micro-slip", as reported by Brown and Honeycombe,<sup>67</sup> and by Paxton *et al.*<sup>68</sup> If polishing occurs by a cutting mechanism, the strains at the actual surface of the zone are probably high, since the surface is virtually a zone of shear fracture. The layer may also have a special structure due to surface heating during polishing. The presence of a layer of this type must probably be accepted as inevitable in any surface prepared by a mechanical method which scratches the surface.

The fact that the polished surface investigated contained a deformed layer of very similar structure to that present on abraded surfaces is considered to be strong evidence that the two processes occur by the same mechanism. Since comparatively small changes in the type and grade of abrasive are unlikely to change fundamentally the polishing mechanism, it seems reasonable to draw the general conclusion that fine metallographic polishing processes occur essentially by a cutting mechanism.

This view was held by the earliest authorities in the field (e.g. Herschel,<sup>69</sup> as quoted by Rayleigh<sup>70</sup>), but in more recent years it has been supplanted by a theory originally advanced by Beilby<sup>1</sup> that polishing occurs by a process of surface flow. The most important single piece of evidence advanced by Beilby in support of his theory is the development of "scratch traces" during the etching of polished surfaces, his explanation for this phenomenon being given in Section VI. However, the Beilby hypothesis is inadequate to account for certain new observations now recorded. Moreover, the whole phenomenon can be explained more simply and more completely by a mechanism consistent with the theory of polishing advanced here, namely, that scratch traces develop as a result of the preferential etching of bands of locally deformed material remaining from the rays of deformation associated with the pre-existing polishing scratches.

A second piece of evidence considered by Beilby to be of major importance was his impression that, during the



polishing of speculum metal on rouged leather, the surface tended to flow over and bridge pre-existing abrasion scratches. Desch<sup>37</sup> has illustrated a similar experiment with bismuth. The flowing action proposed by Beilby was attractive because it was difficult to imagine how otherwise these normally brittle materials could deform during polishing. However, marked plastic deformation can be observed in these materials in an indentation hardness test, as has been demonstrated clearly by Tolansky and Williams.<sup>71</sup> King and Tabor<sup>30</sup> have also shown that plastic deformation occurs during indentation and abrasion of a number of brittle non-metallic materials, such as rock-salt and lead sulphide. Gay and Hirsch<sup>72</sup> found similar evidence of work-hardening in abraded surfaces of calcite. Following the work of Bridgman,<sup>73</sup> King and Tabor suggested that the hydrostatic pressure induced beneath indenting particles is sufficiently high to prevent brittle failure. This obviously could also explain any apparent plastic flow of speculum metal and bismuth during polishing.

Although this mechanism admits that plastic flow of the crests of scratches could occur, it is by no means certain that this was the phenomenon observed by Beilby<sup>1</sup> and by Desch,<sup>37</sup> as their micrographs were not clear enough for unambiguous interpretation. For example, the possibility cannot be ruled out that the effects can be explained by simple geometric considerations of the appearance of two intersecting scratch systems. Plastic smearing undoubtedly can occur during severe abrasion operations, but it is thought that it would be likely only in the most drastic polishing operation.

Surface flow is also often held responsible for failure to detect, in mechanically polished specimens, apparent fine precipitates visible in the same specimens after electrolytic polishing. Although it is easy enough to imagine how, under severe conditions, material may be deformed into depressions in the surface, such as scratches and pits, the author finds it much more difficult to see how material could be picked up and plastically smeared across a second phase. The results of the present author's investigations on this matter, published elsewhere,<sup>74-77</sup> have shown that mechanical polishing, properly conducted, is capable of revealing the finest of optically-resolvable precipitates; moreover, they suggest that many of the effects observed by other workers on electrolytically polished specimens, and believed to be fine precipitates, were etched grooves or pits not associated with optically-resolvable precipitation.<sup>74, 77</sup> In the course of this work, it has been established that the complete absence of fine background scratches or scratch traces is the critical factor for the ready observation of fine precipitation,<sup>76</sup> and it is known that all classical methods of final polishing produce a finely scratched surface.<sup>7</sup> It can be stated, therefore, that there is no real evidence to date that fine particles can be obscured by surface flow during mechanical polishing.

Bowden and Hughes<sup>40</sup> have presented evidence to show that a polishing action is primarily dependent upon the relative melting points of abrasive and specimen. On the basis of this evidence, and in support of the Beilby hypothesis, they suggest that normal rapid polishing processes may be due to surface melting, the molten material being assumed to spread over the surface and

to solidify in the form which Beilby has termed amorphous. The author<sup>7</sup> has confirmed that a general relationship exists between polishing rate and melting point for specimens polished on a diamond-abrasive pad, although many anomalies were found. Moreover, a similar, and even stricter, relationship was found to exist for a definite abrasion stage (the cast alumina-wax lap). Indeed, the polishing conditions used by Bowden and Hughes probably more closely approach a fine abrasion process than a polishing process on the basis of the definitions used in the present paper.

This evidence, then, is not inconsistent with the conclusion reached here that abrasion and polishing occur by the same basic mechanism. However, surface melting can scarcely be expected to play a major part in the removal of large amounts of material, as occurs on a coarse abrasive lap. Furthermore, microscopical examination of the abrasion debris recovered from such a lap shows that the individual particles of the debris are chip-like threads rather than spherical globules (Fig. 26, Plate XII). It seems, therefore, that the relationship between polishing and the relative melting points of abrasive and specimen is more likely to be an indirect one. This possibility was recognized by Bowden and Hughes,<sup>40</sup> who proposed the alternative hypothesis that the critical factor is the reduction in the mechanical properties of the specimen material adjacent to the abrasive particle caused by local heating to relatively high temperatures, but not to the melting point.

The latter proposal is consistent with the present author's proposed mechanism of polishing. It implies that the polishing rate with a particular abrasive will depend upon both the maximum temperature reached at the surface and the mechanical properties of the specimen material at that temperature. Even assuming that the temperature reached is similar, the mechanical properties of various specimen materials at this temperature will be only roughly related to their respective melting points; they may be expected to differ appreciably in their detailed characteristics in this respect, and the results of high-temperature hardness tests, which have been reviewed recently by Westbrook,<sup>78</sup> suggest that this is so. Factors of this type, together with others which determine the actual maximum surface temperature, would account for some of the many anomalies found by the author<sup>7</sup> when relating polishing rate with specimen melting point. It is also reasonable to expect from these considerations that the polishing rate would be an anisotropic property, as the author has observed.<sup>7</sup>

The abrasives commonly used in metallographic practice are much harder and are of considerably higher melting point than the usual specimen materials. It is not clear at this stage which particular properties of the abrasive influence the polishing action. It is possible that the strength of an abrasive particle in the region of its cutting point is always considerably greater than that of the immediately adjoining specimen material, and hence that the particle normally neither fractures nor melts. Other characteristics, such as the frictional properties and the form of the cutting point, may therefore determine the polishing properties. However, when the abrasive and specimen are of more comparable hardness and melting point, as in the rather special conditions of the experiments of Bowden and Hughes,<sup>40</sup> the position may become much more complicated, and factors



other than the cutting action proposed above could become of importance.

Summarizing, it may be said that the metallographic evidence supporting the Beilby theory that polishing occurs by surface flow is far from conclusive. It is, in fact, now less convincing than the theory supported by the present work that fine metallographic polishing operations take place by a cutting mechanism. Since optical methods of examination were used, the present evidence does not, of course, rule out the possibility that a Beilby layer of the type suggested by electron-diffraction evidence<sup>2-4</sup> is present on these surfaces. However, to conform with the new view, this layer would probably have to be imagined as contouring the polishing scratches rather than as being a smear across the surface. Even if it is held that a Beilby layer is present, it still follows that a flowing process can at best make only a minor contribution to the polishing processes under consideration. Finally, there is now no good reason to suppose that a layer of this type would interfere with the examination of polished surfaces by optical microscopy.

The skidding method of polishing on magnesium oxide developed by the author<sup>7</sup> may form an exception to the general theory. Since this process does not produce optically detectable scratches, it can scarcely occur by a

cutting process. It is well known that, when a definite etching reagent is incorporated in the abrasive paste ("polish-attack"), metal removal takes place essentially by chemical attack, and it is suggested tentatively that a similar mechanism may operate in the case of the skidding magnesium oxide pad. In this event, the etching must result from attack by the water itself or from the oxygen in solution in the water, the abrasive serving essentially to remove continuously any protective films present originally or formed during the attack, thus both accelerating the rate of attack and making it more uniform. Grebenshikov<sup>79,80</sup> has suggested that a mechanism of this type may operate during the polishing of glass, although he advanced this theory as a general one rather than as a special case, as proposed here. Nevertheless, if such a mechanism does exist, it is conceivable that it may contribute to some extent to other polishing processes which occur mainly by cutting.

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## SYNOPSIS

In the uranium-palladium system the liquidus shows a eutectic between uranium and UPd at  $998^{\circ} \pm 3^{\circ} \text{C.}$ , a maximum corresponding to the formation of  $\text{UPd}_3$  at approximately  $1640^{\circ} \text{C.}$ , and a minimum at  $1305^{\circ} \pm 5^{\circ} \text{C.}$  and 72 wt.-% palladium. The compound  $\text{U}_5\text{Pd}_6$  forms by peritectic reaction from  $\text{UPd}_3$  at  $1110^{\circ} \pm 10^{\circ} \text{C.}$ , and the compound UPd by peritectic reaction from  $\text{U}_5\text{Pd}_6$  at  $1047^{\circ} \pm 7^{\circ} \text{C.}$   $\text{U}_5\text{Pd}_6$  decomposes into UPd and  $\text{UPd}_3$  at  $980^{\circ} \pm 5^{\circ} \text{C.}$  and UPd decomposes into uranium and  $\text{UPd}_3$  at  $970^{\circ} \pm 5^{\circ} \text{C.}$  Palladium depresses the  $\gamma \rightleftharpoons \beta$  uranium transformation to  $756^{\circ} \pm 4^{\circ} \text{C.}$ , but leaves the  $\beta \rightleftharpoons \alpha$  transformation unaffected. The maximum solubility of palladium in  $\gamma$ -uranium is 2.3 wt.-%, but the solubility is less than 0.14 wt.-% in the  $\beta$  and  $\alpha$  forms. Palladium dissolves up to 38 wt.-% uranium in the  $\delta$  solid solution, which forms from  $\text{UPd}_3$  by peritectic reaction.

The crystal structure of  $\text{UPd}_3$  is of the type  $\text{Do}_{24}$ .

## I.—INTRODUCTION

THE investigation of the uranium-palladium system described formed part of a programme for the study of binary uranium alloys sponsored by the United Kingdom Atomic Energy Authority.

Uranium exists in the solid state in three allotropic modifications:  $\alpha$ , which is orthorhombic<sup>1</sup> and occurs from room temperature to  $665^{\circ} \pm 3^{\circ} \text{C.}$ ; the complex tetragonal  $\beta$  structure,<sup>2</sup> stable from  $665^{\circ}$  to  $772^{\circ} \pm 3^{\circ} \text{C.}$ ; and the body-centred cubic  $\gamma$  form, which is found from  $772^{\circ}$  to the melting point at  $1133^{\circ} \text{C.}$  The closest distance of approach in the latter structure (3.0 Å.) is taken as the atomic diameter for size-factor considerations.

Palladium is face-centred cubic between room temperature and the melting point at  $1552^{\circ} \text{C.}$  The closest distance of approach is 2.75 Å.

No previous work on this system was available at the time the investigation was begun.

## II.—EXPERIMENTAL

## 1. PROCEDURE

(a) *Materials Used*

The uranium, which was supplied by the Atomic Energy Research Establishment, was more than 99.95% pure. The balance consisted principally of nitrogen, carbon, iron, aluminium, silicon, and manganese. The palladium was obtained from Messrs. Johnson, Matthey and Co., Ltd., and its purity was also higher than 99.95%, the balance being mainly platinum.

(b) *Preparation of the Alloys*

In preliminary work on the system, the alloys were prepared by melting the charges *in vacuo* in zirconia crucibles. Heating was carried out in a high-frequency induction furnace, and alloying was accompanied by a considerable evolution of heat, especially at compositions near the compound  $\text{UPd}_3$ . Chemical analysis showed the alloys to be contaminated with zirconium,

as much as 0.5 wt.-% being present in alloys of approximately equiatomic proportions. Beryllia crucibles were attacked to much the same extent during alloying, but alloys prepared in an arc furnace having a water-cooled copper hearth and remelted in beryllia crucibles in the induction furnace, contained very little beryllium, and all alloys were subsequently prepared in this manner. The second melting in the induction furnace ensured uniformity of composition.

(c) *Metallographic Examination*

After being ground on successively finer emery papers, lubricated with paraffin, the alloys were polished on Selvyt cloth coated with a suspension of diamond dust in paraffin. In some cases the uranium-rich alloys were finished electrolytically, and for this purpose a bath containing equal proportions of phosphoric acid, ethyl alcohol, and ethylene glycol was used. This process required only a few seconds at 20 V. It was found extremely difficult to prepare metallographic specimens from alloys containing a high proportion of the compound  $\text{UPd}_3$ , since pieces tended to break away from the surface during grinding and polishing.

Uranium-rich alloys were etched with one of the following three reagents: (i) 50% nitric acid in water; (ii) a mixture of 20% nitric acid and 10% hydrochloric acid in water; or (iii) steam. Etching times were of the order of a few seconds. These reagents attacked the uranium preferentially and increased the contrast between UPd and  $\text{U}_5\text{Pd}_6$ ; these compounds were also visible unetched. Palladium-rich alloys were considerably more difficult to attack, the nitric-hydrochloric acid reagent requiring a minute or two to work. Some success was obtained with these alloys by using a mixture of equal parts of 20% potassium cyanide and 20% ammonium persulphate.

(d) *Thermal Analysis*

For thermal analysis, 70–100 g. of alloy contained in a beryllia crucible were heated *in vacuo* in a high-

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frequency induction furnace.<sup>3</sup> The platinum/platinum-rhodium thermocouple was protected by a beryllia-coated alumina sheath, and inverse-rate thermal curves were obtained by means of an automatic potentiometer and a plotting chronograph. The rate of cooling was adjusted to about  $10^{\circ}\text{C./min.}$  at  $1400^{\circ}\text{C.}$

The transformation temperatures of uranium, the eutectic arrests, and most of the liquidus points were easily detected on both heating and cooling curves. Results for alloys containing 30–35 wt.-% palladium, however, were unsatisfactory, since irregular cooling caused by the peritectic reactions resulted in a bulge on the curves which extended over a temperature range, rather than in a sharp peak. Such curves have been disregarded in drawing the diagram.

#### (e) Heat-Treatment

Alloys intended for heat-treatment were sealed in evacuated silica tubes, and reaction between the alloy and the silica during annealing was prevented either by enclosing the specimen in an alumina tube or by wrapping it in tantalum foil. In no case did the tantalum adhere to the specimen, except when the alloy was partly or entirely molten. Long-period annealing at temperatures up to  $1100^{\circ}\text{C.}$  was carried out in horizontal resistance furnaces controlled to  $\pm 3^{\circ}\text{C.}$  The alloys were quenched from these furnaces by hand into water; the silica tubes either shattered immediately or were broken under the surface.

For short periods of 1 or 2 hr. at temperatures up to  $1425^{\circ}\text{C.}$ , annealing was performed *in vacuo* in a vertical platinum-wound furnace, hand-controlled to  $\pm \frac{1}{2}^{\circ}\text{C.}$  A specimen wrapped in tantalum and contained in an alumina crucible was suspended by molybdenum wire from the top of the furnace. A measuring thermocouple was placed with its hot junction in contact with the specimen. At the end of the annealing period the furnace was filled with argon, a fuse blown, and the whole assembly with the exception of the thermocouple dropped into a water-bath. No appreciable alteration of temperature was recorded on the thermocouple during the quenching operation.

All alloys were given a preliminary anneal of 1 month at  $970^{\circ}\text{C.}$  Subsequent annealing times depended upon the composition of the alloys and on the temperature. It was found that 3–4 months were necessary to obtain equilibrium with alloys containing UPd and  $\text{U}_5\text{Pd}_6$ , and this period was also given to alloys annealed at  $800^{\circ}\text{C.}$  and below. In the region 35–50 wt.-% palladium long-period annealing caused progressive loss of uranium, and the proportion of  $\text{UPd}_3$  present in the alloys increased. For the determination of solidus temperatures trial showed that 1 hr. was more than sufficient.

#### (f) X-Ray Methods

Most of the alloys were extremely brittle, and powder specimens were prepared by crushing a clean fragment of an annealed alloy either in an agate mortar under alcohol, or in a steel percussion mortar. The powder patterns obtained after this operation had sharp doublets, and no further heat-treatment was necessary. Filings from homogenized ingots of the ductile phase based on

the palladium solid solution were annealed in evacuated silica tubes at the temperature of homogenization, and the lattice parameters of the quenched specimens were determined by standard extrapolation methods. The photographs were taken with either a 9- or 19-cm. Unicam camera, using cobalt  $K_{\alpha}$  radiation.

It was not found possible to obtain powder patterns sufficiently strong for reliable phase identification from alloys containing UPd or  $\text{U}_5\text{Pd}_6$ . The glancing-angle method on the annealed lump alloys also proved unsatisfactory because of the large grain-size of the specimens. Consequently, the existence of these two phases was established with the aid of the microscope.

The structure of  $\text{UPd}_3$  was fixed by the powder method and by single-crystal rotation photographs. Suitable well-formed single crystals for the latter technique were hand-sorted from the residue from a slowly-cooled ingot, containing 40 wt.-% palladium, after electrolytic extraction in dilute hydrochloric acid.

#### (g) Chemical Analysis

The palladium was precipitated with dimethylglyoxime and weighed as the complex. The uranium was weighed as the oxide. In most cases only the palladium was determined, although for some critical alloys and in order to check the accuracy of the method, both elements were determined. The sum of the percentages lay between 99.88 and 100.06. Analyses were carried out on clean samples cut or broken from the centre of the annealed alloys, the specimens being those actually examined under the microscope.

## 2. RESULTS\*

The equilibrium diagram is shown in Fig. 1. All the thermal-curve ingots and a number of the micro-specimens prepared separately for annealing treatment were analysed; the analysed micro-specimens are represented by full circles and triangles.

#### (a) The Liquidus

The liquidus curve falls from the melting point of uranium at  $1133^{\circ}\text{C.}$  to a eutectic between  $\gamma$ -uranium and UPd at  $998^{\circ} \pm 3^{\circ}\text{C.}$  and 21.1 wt.-% palladium. Fig. 2 (Plate XIII) shows the structure of a slowly-cooled alloy containing 10.0 wt.-% palladium. The composition of the eutectic point was bracketed by furnace-cooling a series of alloys with compositions ranging from 14.0 to 26.0 wt.-% palladium, and examining the ingots under the microscope. Primary uranium was present at 20.9 and primary UPd at 21.4 wt.-% palladium. It was noted that furnace-cooling was sufficiently slow for the eutectic structure to coarsen and the UPd needles to decompose. The same technique was adopted in order to find the ends of the peritectic horizontals corresponding to the formation of UPd,  $\text{U}_5\text{Pd}_6$ , and  $\delta$  (see below).

From the eutectic point, the liquidus rises to meet the peritectic reaction liquid +  $\text{U}_5\text{Pd}_6 \rightleftharpoons \text{UPd}$  at a composition shown by slow cooling to lie between 28.0 and 30.0 wt.-% palladium, and at a temperature shown by annealing to be  $1047^{\circ} \pm 7^{\circ}\text{C.}$ , and to meet the peritectic reaction liquid +  $\text{UPd}_3 \rightleftharpoons \text{U}_5\text{Pd}_6$  between 34.0 and

\* Tables showing details of the experimental results have been deposited in the Joint Library of the Iron and Steel Institute and the Institute of Metals.



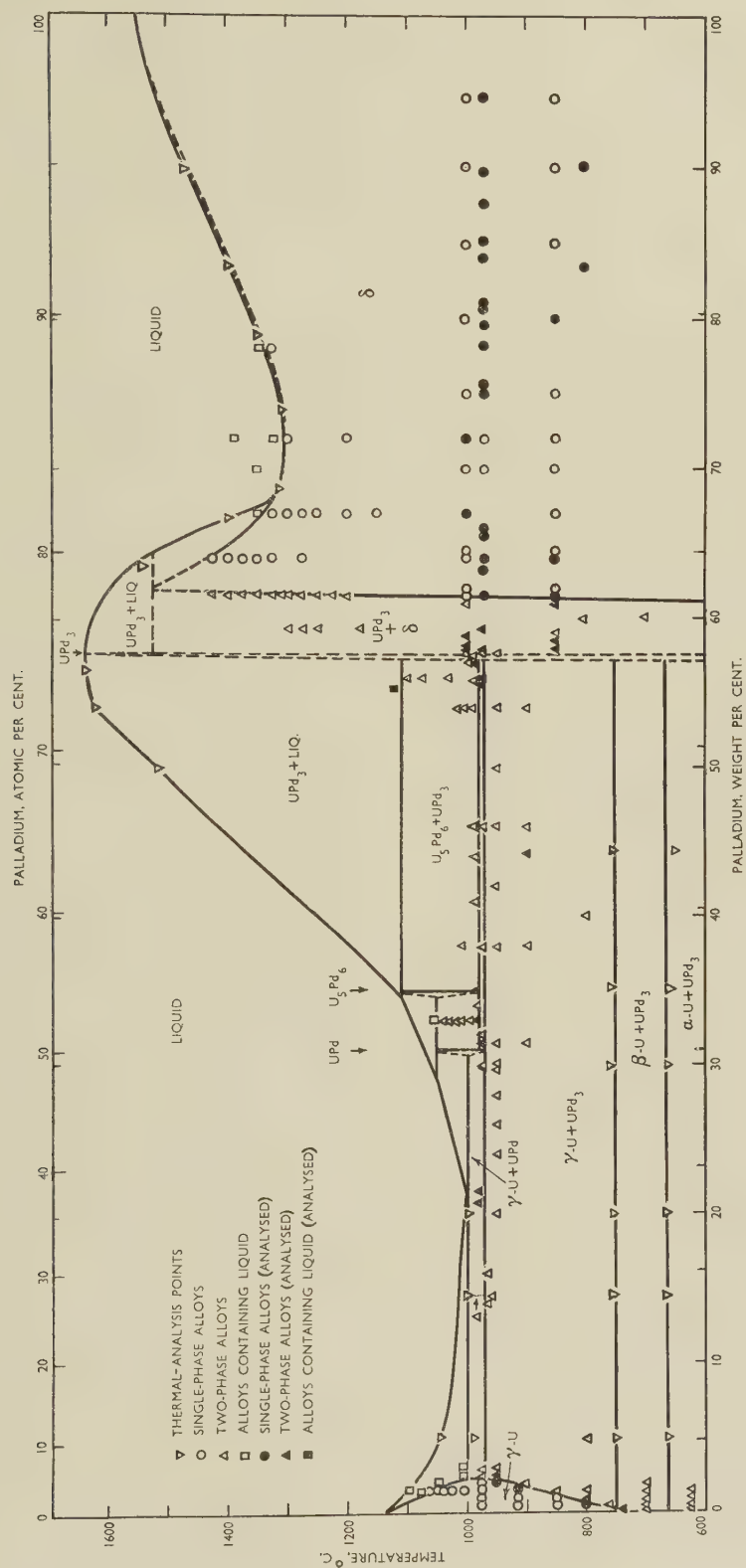


Fig. 1.—The Equilibrium Diagram of the Uranium-Palladium System.

35.0 wt.-% palladium and at  $1110 \pm 10^\circ \text{C}$ . A maximum point occurs at approximately  $1640^\circ \text{C}$ . at the compound  $\text{UPd}_3$ , and a minimum point at  $1305^\circ \pm 5^\circ \text{C}$ . at about 72 wt.-% palladium. The liquidus intersects the horizontal corresponding to liquid +  $\text{UPd}_3 \rightleftharpoons \delta$  between 64.0 and 66.0 wt.-% palladium, but the temperature of this reaction has not been established, since it was too high for annealing and quenching to be carried out with the furnace available.

With increasing palladium content, the liquidus rises from the minimum to the melting point of pure palladium at  $1552^\circ \text{C}$ .

#### (b) *The Solubility of Palladium in Uranium*

The  $\alpha$ ,  $\beta$ , and  $\gamma$  solubility boundaries were determined microscopically. Some solubility of palladium occurs in the  $\gamma$  modification of uranium, the maximum value being about 2.3 wt.-% at the eutectic temperature of  $998^\circ \text{C}$ . From this point the solubility decreases with temperature until, at  $760^\circ \text{C}$ ., it is less than 0.5 wt.-%. In the  $\beta$  and  $\alpha$  forms, the solubility is less than 0.14 wt.-% at all temperatures down to  $625^\circ \text{C}$ . Fig. 3 (Plate XIII) shows a 2.02 wt.-% palladium alloy, solution-treated at  $970^\circ \text{C}$ . in the  $\gamma$  field, and annealed for 41 hr. at  $700^\circ \text{C}$ . A fine precipitate of  $\text{UPd}_3$  is present in a matrix of uranium.

Thermal analysis showed that the  $\gamma \rightleftharpoons \beta$  transformation is depressed by the addition of palladium to  $756 \pm 4^\circ \text{C}$ ., whilst the  $\beta \rightleftharpoons \alpha$  transformation is unaffected. It was not found possible to suppress the change from  $\gamma$ - to  $\alpha$ -uranium by quenching.

The solidus curve descends smoothly from the melting point of uranium to meet the eutectic horizontal at  $998 \pm 3^\circ \text{C}$ . and 2.3 wt.-% palladium.

#### (c) *The Compounds UPd and $\text{U}_5\text{Pd}_6$*

The existence of two compounds was established microscopically, because the unsatisfactory nature of the powder photographs from these compounds prevented reliable phase identification and also the determination of the structures by X-ray methods.

The compound UPd (30.9 wt.-% palladium) was bracketed between the compositions 30.0 and 31.5 wt.-% palladium at  $975^\circ \text{C}$ . From the proportions of the phases in these two alloys, UPd dissolves very little uranium or palladium. Heat-treatment at successively higher temperatures of an alloy containing 33.0 wt.-% palladium and consisting of UPd and  $\text{U}_5\text{Pd}_6$  (Fig. 4, Plate XIII) showed that this compound forms between  $1040^\circ$  and  $1054^\circ \text{C}$ .

Primary crystals of UPd occur as long needles, and Fig. 5 (Plate XIII) shows an alloy after rapid cooling in the arc furnace. It was noticed, however, that slowly cooling an alloy containing these needles was sufficient to cause decomposition to take place, with the formation of uranium and  $\text{UPd}_3$  (Fig. 6, Plate XIII). The temperature of this decomposition was shown by annealing to lie between  $968^\circ$  and  $975^\circ \text{C}$ . Above this temperature UPd exists in equilibrium with either  $\gamma$ -uranium (Fig. 7, Plate XIII) or with  $\text{UPd}_3$ .

The compound  $\text{U}_5\text{Pd}_6$  (34.9 wt.-% palladium) forms by peritectic reaction from  $\text{UPd}_3$  at a temperature also shown by annealing to lie between  $1100^\circ$  and  $1120^\circ \text{C}$ . When it occurs in the primary state, it forms long needles which can be distinguished from UPd in slowly-cooled

alloys by the absence of any decomposition (Figs. 8 and 9, Plate XIV). Like UPd, it exists over a narrow range of homogeneity, since two alloys containing 34.0 and 35.0 wt.-% palladium respectively, annealed at  $985^\circ \text{C}$ ., were on either side of the composition of the compound. The proportions of the phases were such that the alloy with 35.0 wt.-% palladium was practically single-phase. At this temperature  $\text{U}_5\text{Pd}_6$  exists in equilibrium with either UPd (Fig. 4), or  $\text{UPd}_3$  (Fig. 10, Plate XIV). It decomposes between  $975^\circ$  and  $985^\circ \text{C}$ . into UPd and  $\text{UPd}_3$ .

#### (d) *The Compound $\text{UPd}_3$*

The formation of  $\text{UPd}_3$  was always accompanied by a considerable evolution of heat. It occurs at a maximum on the liquidus curve which thermal analysis showed to be about  $1640^\circ \text{C}$ . In alloys containing more uranium than the stoichiometric composition, the compound exhibits extremely well-developed crystals, relatively unattacked by the peritectic reaction  $\text{UPd}_3 + \text{liquid} \rightleftharpoons \text{U}_5\text{Pd}_6$  and usually having an hexagonal section in the microstructures. In alloys richer in palladium, the reaction  $\text{UPd}_3 + \text{liquid} \rightleftharpoons \delta$  destroys the regular shape of the crystals (Fig. 11, Plate XIV).

$\text{UPd}_3$  is stable down to at least  $620^\circ \text{C}$ ., and below  $970^\circ \text{C}$ . exists in equilibrium with the uranium or palladium ( $\delta$ ) solid solutions. The crystal structure was determined by both rotation and powder photographs. It was found to be hexagonal, of the structure type  $\text{Do}_{24}$ , and isomorphous with  $\text{TiNi}_3$  and  $\text{TiPd}_3$ . The observed and calculated intensities derived from a powder pattern of this compound are available in the data deposited in the Institute library. Heal and Williams<sup>4</sup> also found this structure for  $\text{UPd}_3$ . Since  $\text{TiPd}_3$  and  $\text{UPd}_3$  are isomorphous, it was considered possible that titanium might replace uranium in the lattice, and an alloy of nominal composition  $\text{U}_4\text{Ti}_1\text{Pd}_3$  was prepared. This alloy was practically single-phase after preparation in the arc furnace.

The parameters of  $\text{UPd}_3$  in two-phase alloys containing excess uranium differed from those in alloys containing excess palladium. Specimens quenched from  $975^\circ \text{C}$ ., when saturated with uranium, gave values of  $c = 9.64(1)$  and  $a = 5.76(9) \text{ \AA}$ ., with  $c/a = 1.671$ , whereas those quenched from  $1180^\circ \text{C}$ . when saturated with palladium gave values of  $c = 9.52(6)$ ,  $a = 5.76(3) \text{ \AA}$ ., with  $c/a = 1.653$ . The parameters were calculated from the high-angle lines only. The change in lattice parameter with increasing palladium content is accompanied by a marked separation in the powder photographs between the pairs of lines 402 and  $\begin{Bmatrix} 008 \\ 207 \end{Bmatrix}$ , 406 and 209, and 422 and  $\begin{Bmatrix} 407 \\ 228 \end{Bmatrix}$ , whilst the lines corresponding to the overlapping pairs 401 and 224, and 201 and 004, are broadened.

It may be concluded, therefore, that  $\text{UPd}_3$  exists over a small solubility range. The parameters given by Heal and Williams were  $c = 9.621$  and  $a = 5.757 \text{ \AA}$ .

#### (e) *The Palladium Solid Solution $\delta$*

The  $\delta$  solid solution forms by a peritectic reaction from  $\text{UPd}_3$ , the liquidus falling to a minimum with increasing palladium content. It was not found possible to fix the temperature of the peritectic reaction, although annealing was carried out up to  $1425^\circ \text{C}$ . By extrapolating the solidus and solid-solubility curves, and



knowing that primary  $\text{UPd}_3$  disappears in slowly-cooled alloys between 64.0 and 66.0 wt.-% palladium, it is estimated that this temperature is about 1525° C.

The position of the minimum on the solidus and liquidus curves was established by heat-treatment and by thermal analysis. Since the solidus and liquidus curves lie very close to each other in this region, successive annealing treatments eventually resulted in alloys which appeared to have been completely molten, and which were unsuitable for metallographic examination. It is possible, therefore, that in one or two cases the alloys were not entirely molten, although they have been assumed to be so in drawing the curves. Such errors would not appreciably alter the position of the solidus and liquidus curves.

Uranium dissolves to a considerable extent in palladium, and Fig. 12 (Plate XIV) shows a single-phase alloy containing 64.0 wt.-% palladium annealed at 1425° C. The position of the  $\delta$  solid-solubility boundary was determined both by microscopical examination and by measurement of the lattice parameters. The lattice parameter/composition curve was constructed from alloys quenched from 970° C., and the parameters of two-phase alloys were determined by quenching from temperatures up to 1400° C. The solubility decreases slightly with increase in temperature, which is an unusual feature, and the boundary lies at 61.1 wt.-% palladium at 700°, 800°, and 900° C., at 61.4 wt.-% at 1180° C., and at 61.6 wt.-% at 1400° C. Fig. 13 (Plate XIV) shows a two-phase alloy containing 61.6 wt.-% palladium after annealing at 1425° C. Some loss of palladium has evidently occurred from this specimen, since the parameter of  $\delta$  in this alloy at 1400° C., at which temperature it was also two-phase, showed the boundary to lie at 61.6 wt.-% palladium.

The  $\delta$  solid solution containing up to about 15 wt.-% uranium is quite ductile, and it was possible to hot roll an alloy of this composition down to 0.008 in. The rolling was performed on a button heated to 800° C. in air, and reheated to this temperature after every two passes, each pass resulting in some 20% reduction. Using this technique, however, it was not possible to roll alloys richer than 20% in uranium without the specimens crumbling. Some surface oxidation occurred during heating at 800° C. and the specimens became covered with a dark-grey film. The attack was less marked at lower temperatures, and a clean sample annealed in air at 500° C. for 17 hr. only turned a faint blue.

### III.—DISCUSSION

The size-factor of palladium with respect to uranium is 8.3%, and uranium with respect to palladium 9.1%.

These values are obtained using the closest distance of approach in  $\gamma$ -uranium. It is evident, therefore, that the terminal solid solutions cannot be interpreted from size-factors alone, as these would not account for the considerable difference between the  $\gamma$  and  $\delta$  solid solubility ranges. The extensive solubility of uranium in palladium is unusual, since, from free-energy considerations, the presence of a stable compound with a high-melting-point maximum such as  $\text{UPd}_3$  would be expected to restrict the solid solubility.

An interpretation of the alloying characteristics based on electronic factors is difficult, since the effective electron contribution of both elements probably varies with the crystal structure. The outer electrons of the free uranium atom exist either in the state  $(7s)^2(6d)^1(5f)^3$  or in the state  $(7s)^2(6d)^4$ . From a calculation of the volume of the Brillouin zones of the orthorhombic and body-centred cubic forms of the element, Raynor<sup>5</sup> concludes that it may be behaving with valencies of four and six, respectively, in these structures. In either case, the solubility of palladium would be expected to be small.

In the solid state the outer electrons of palladium are considered to occupy overlapping bands of mainly 4d and 5s type, with 0.6 holes remaining in the 4d band. Measurements of certain of the physical properties, such as the lattice parameter, paramagnetic susceptibility, thermoelectric power, and electrical resistivity, enable the effective electron contribution of the uranium in the  $\delta$  solid solution to be estimated. The results of these measurements will be published elsewhere.

The electronic structure of nickel in the solid state is similar to that of palladium, but with overlapping 3d and 4s bands. A comparison between the uranium-nickel and uranium-palladium diagrams, however, is complicated by the unfavourable size-factor of nickel with respect to uranium.

### ACKNOWLEDGEMENTS

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# 1722 SOME EXPERIMENTS ON THE DETERMINATION OF THE LATENT HEATS OF TRANSITION OF TITANIUM AND IRON\*

By T. H. SCHOFIELD,† M.Sc., F.I.M., MEMBER  
(Communication from the National Physical Laboratory)

## SYNOPSIS

The latent heats of the  $\alpha \rightarrow \beta$  transition in titanium and the  $\alpha \rightarrow \gamma$  transition in iron have been determined by a method which depends on the constancy of the products of the rates of heating and the times of transformation, and a knowledge of the specific heats. The result obtained for iron (218 cal./g.-atom) agrees well with accepted values; that for titanium (813 cal./g.-atom) is more closely in accordance with a recently determined value by Backhurst (880 cal./g.-atom) than with one derived earlier by McQuillan (680 cal./g.-atom).

## I.—INTRODUCTION

DURING the course of some experiments on the determination of the temperature of the  $\alpha \rightarrow \beta$  transition in titanium-oxygen alloys by means of time/temperature heating curves, it was observed that the product of the rate of heating and the time of the arrest of a specimen of titanium was approximately constant. Application of this observation to the experimental results showed that the latent heat of transition could be estimated if the specific heat of titanium at the transition temperature were known. At the time, no measured data on the specific heat of titanium at the transition temperature were available. Recently, the specific heat of titanium up to about 1080° C. and also the latent heat of transition have been accurately determined by Backhurst,<sup>1</sup> working with a large specimen of commercially pure material. These values for the specific heat have been used in the present series of experiments. A redetermination of the latent heat of transition of  $\alpha \rightarrow \gamma$  iron has also been made, since the specific heat of iron at the transition temperature is known.<sup>2, 3</sup>

## II.—EXPERIMENTAL METHOD

Two samples of titanium, one manufactured by the New Jersey Zinc Co.† and one by Imperial Chemical Industries, Ltd., Metals Division,† and a sample of pure iron prepared in the Metallurgy Division of the National Physical Laboratory, were used in the experiments. Cylindrical specimens were used, approximately 19 mm. long and 8 mm. in dia. An axial hole, 10 mm. deep and 1.6 mm. in dia., was drilled in each specimen for the insertion of a thermocouple. The weights were: titanium (N.J.Z.) 4.038 g., titanium (I.C.I.) 3.737 g., iron 7.044 g.

Each specimen was supported vertically in a furnace on a twin-bore silica sheath which was pushed into the axial hole. A 0.2-mm.-dia. platinum/platinum-10% rhodium thermocouple was threaded through the silica sheath, the junction of the couple being bare and in direct contact with the end of the hole in the specimen.

The weights of the couple and sheath within the specimen were approximately 0.011 and 0.018 g., respectively; consequently, the heat capacity of the couple and sheath was small compared with that of the specimen.

The furnace consisted of a spiral of tungsten wire enclosed in a series of molybdenum radiation screens, the whole being in a vacuum. Details of the furnace have been given elsewhere.<sup>4</sup> The thermocouple wires were led out through the base of the furnace to a cold junction and thence to a Tinsley vernier potentiometer on which most of the e.m.f. of the couple was balanced,



FIG. 1.—Heating Curve for Titanium Specimen. Mean rate of heating = 6.9° C./sec.

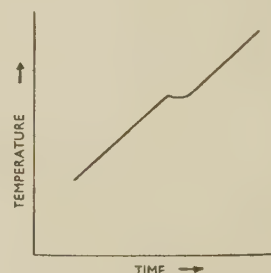


FIG. 2.—Heating Curve for Iron Specimen. Mean rate of heating = 3.4° C./sec.

the remainder of the e.m.f. in the range required being fed to a Tinsley D.C. amplifier and recorder which traced out the time/e.m.f. curves. The rates of heating and the times of the arrests were measured from the curves by means of a protractor and a millimetre scale, respectively. The rates of heating were between about 1.7° and 26° C./sec. If slower or faster rates of heating were used, the measurement of times of arrests and rates of heating was rendered difficult. Figs. 1 and 2 show typical time/e.m.f. curves for titanium and iron, respectively. It will be noticed that the titanium arrest is not parallel to the time axis, i.e. the arrest does not occur isothermally. The probable reasons for this are discussed in the next section, and a correction based on these assumptions has been applied. The iron

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‡ Referred to hereafter as N.J.Z. and I.C.I. titanium.



arrests showed signs of a slight amount of superheating, but the average slopes of these arrests were zero, and no correction was necessary. It is probable that the apparent superheating is associated with the two peaks observed in the transformation by Awbery and Griffiths.<sup>3</sup>

The transition temperatures of the N.J.Z. and I.C.I. titanium specimens, as indicated by the end of the arrest on the heating curves, were 885° and 911° C., respectively, at a heating rate of about 3° C./sec. The transition temperatures rose with the rate of heating, the corresponding temperatures being 902° and 930° C. at a heating rate of 20° C./sec. The temperature ranges of the transition for the N.J.Z. and I.C.I. specimens were approximately 22° and 50° C., respectively. The higher temperature of the end of the transition, and the greater range of temperature of transition, of the I.C.I. specimen are attributed to its higher impurity content. The transition temperature of the iron specimen was 914° C. at a heating rate of 2° C./sec.; this increased to 930° C. at a heating rate of 14° C./sec. The range of transformation was 5° C.

The results of the experiments show that  $\frac{d\theta}{dt} \cdot t'$  is approximately constant for a given specimen, so that if  $\frac{d\theta}{dt}$  is plotted against  $\frac{1}{t'}$ , a straight line of slope  $\frac{d\theta}{dt} \cdot t'$  is obtained; consequently,  $L_t$  can be calculated from (1) if  $C_p$  is known.

If the arrest occurs over a range of temperature, it is inferred that this is due to the effect of impurities and/or the thermal lag in the specimen. It is considered that both these factors may operate in the case of the titanium specimens, as they were relatively less pure than the iron specimen, and since the thermal conductivity of titanium is much lower than that of iron. The effect of either of these factors would be to cause the arrest to take place over a range of temperature because the specimen is absorbing heat at a greater rate than is required for the proportion of  $\alpha$  which is transforming to  $\beta$ . The amount of this extra heat is proportional to the mean slope of the arrest. Consequently, the amount of heat

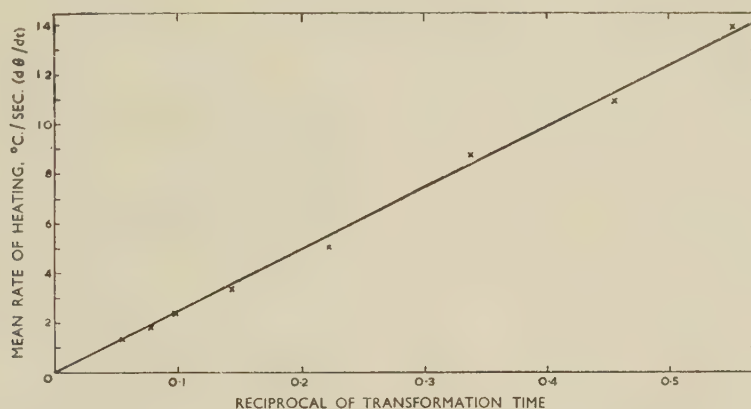


FIG. 3.—Mean Rates of Heating Plotted Against Reciprocals of the Times of Transformation (sec.) for Pure Iron.

#### Method of Estimation of Heat of Transition

Let  $L_t$  = heat of transition (cal./g.-atom)

$m$  = mass of specimen (g.)

$t'$  = duration of arrest (sec.)

$C_p$  = mean specific heat at the transition temperature (cal./g./°C.)

$A$  = Atomic weight of the metal

$\frac{d\theta}{dt}$  = mean of rates of heating before and after the transition (°C./sec.)

$\frac{d\theta'}{dt}$  = slope of the arrest (°C./sec.)

$C_{p(a)}$  = atomic heat at the transition temperature

Since the time of the arrest is proportional to the heat absorbed by the specimen and the amount of heat supplied depends on the rate of heating and the time during which the heat is applied, then for isothermal arrests:

$$\frac{mL_t}{A} = \frac{d\theta}{dt} \cdot t' m C_p$$

$$L_t = \frac{d\theta}{dt} \cdot t' C_p A \quad (1)$$

$$L_t = k C_{p(a)} \quad (2)$$

where  $k$  is a constant.

for isothermal transformation is less than that given by

(1) by  $\frac{d\theta'}{dt} \cdot t'$ . Equation (1) then becomes:

$$L_t = \left( \frac{d\theta}{dt} t' - \frac{d\theta'}{dt} t' \right) C_p A \quad (3)$$

$$= (k - k') C_{p(a)} \quad (4)$$

### III.—RESULTS

Figs. 3 and 4 show the results of the experiments on iron and titanium, respectively, in which the mean rates of heating are plotted against the reciprocals of the times of transformation. In Fig. 4, part of the curve for iron is plotted on the same scale as the titanium results for purposes of comparison. Fig. 5 shows the mean slopes of the arrests of the titanium specimens plotted against the reciprocals of the times of the arrests.\* The specific heat of iron at the transition temperature (908° C.) is 0.158 cal./g./°C.<sup>2</sup> and the mean of the specific heats of titanium at the beginning (0.165 cal./g./°C.) and end (0.143 cal./g./°C.) of the transition is 0.154 cal./g./°C.<sup>1</sup> Substituting these values and the corresponding slopes

\* The mean slopes of the arrests  $\times 10$  are plotted for convenience.

of the curves from Figs. 3, 4, and 5 in equations (1) and (3) gives the following results:

Iron

$$L_t = 24.7 \times 0.158 \times 55.8 = 218 \text{ cal./g.-atom}$$

Titanium (N.J.Z.)

$$L_t = (134 - 23.6) \times 0.154 \times 47.9 = 814 \text{ cal./g.-atom}$$

Titanium (I.C.I.)

$$L_t = (158 - 48) \times 0.154 \times 47.9 = 811 \text{ cal./g.-atom}$$

The heat of transition of  $\alpha \rightarrow \gamma$  iron has been determined by many workers, and values between 160 and 375 cal./g.-atom have been reported.<sup>5</sup> Kubaschewski<sup>6</sup> suggests a value of 220 cal./g.-atom after consideration of the results of many investigations. This agrees with the determination of Awbery and Griffiths<sup>3</sup> (218 cal./g.-atom) and of Backhurst.<sup>2</sup>

Until Backhurst<sup>1</sup> recently determined the value (880 cal./g.-atom),† no direct determinations of the heat of transition of  $\alpha \rightarrow \beta$  titanium appear to have been carried out. Kelley<sup>7</sup> gave an estimated figure of 950 cal./g.-atom based on the specific-heat measurements

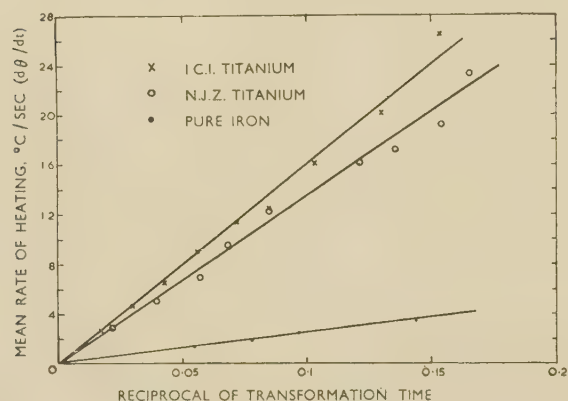


Fig. 4.—Mean Rates of Heating Plotted Against Reciprocals of the Times of Transformation (sec.) for Pure Iron and Titanium.

of Jaeger, Rosenbohm, and Fonteyne,<sup>8</sup> and McQuillan<sup>9</sup> derived a value (670 cal./g.-atom) from thermodynamic data obtained during a study of the titanium-hydrogen system.<sup>9</sup> The result reached in the present work is thus

† The probable accuracy of the results is difficult to estimate, but it is considered that Backhurst's results are accurate to within  $\pm 5\%$  and the present author's to within  $\pm 10\%$ .

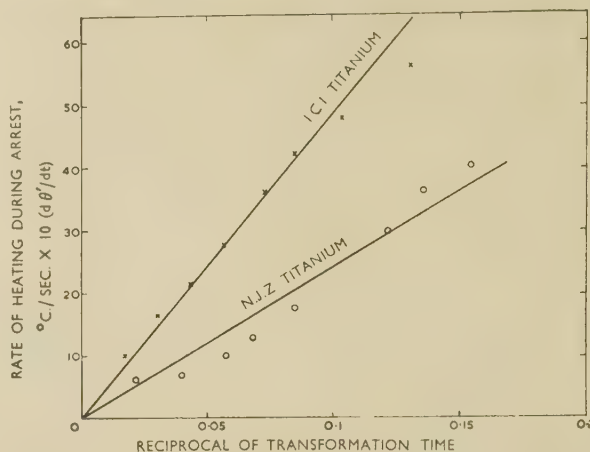


Fig. 5.—Mean Slopes of Arrests of Titanium Specimens Plotted Against Reciprocals of the Times of the Arrests (sec.).

in better agreement with the direct determination by Backhurst.

#### ACKNOWLEDGEMENTS

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# THE BEHAVIOUR OF INTERFACES IN LIGHTLY WORKED URANIUM DURING RECRYSTALLIZATION\*

1723

By P. E. MADSEN,† B.Sc., MEMBER

## SYNOPSIS

The boundaries of twins and kinks in uranium appear to possess an appreciable surface energy, and on annealing they undergo alterations which would be expected from a tendency to reduce the surface area. Phenomena such as twins becoming free from grain boundaries, twins becoming joined over part of their length, and strain-induced boundary migration are readily explained on this basis.

## I.—INTRODUCTION

THE recrystallization of uranium after cold work has recently been the subject of several papers.<sup>1-4</sup> In these and other papers the important role played by twins during recrystallization was emphasized. Mott and Haines<sup>5</sup> observed that twins broadened in places on annealing and that nuclei formed at the junctions of interpenetrating twins. Cahn<sup>6</sup> reported that {130}- and {172}-twins became free from grain boundaries and that the latter also became joined in places on annealing. In heavily deformed uranium, Cabane<sup>1</sup> observed that twins were sometimes absorbed by the matrix grain and sometimes by neighbouring grains. The author<sup>3</sup> has found that nuclei are associated with twins, particularly where they intersect other twins, kink bands, or boundaries.

The present paper contains microstructural observations, made during a study of the annealing of rolled uranium sheet, which suggest that nearly all the changes can be explained in terms of the reduction of interfacial energy, as in normal grain growth.

For purposes of discussing the microstructures, they have been regarded as coming from a two-dimensional material. In most cases the results deduced will probably not be very far wrong, but the presence of unexpected features near the plane of sectioning may lead to apparently anomalous behaviour in some cases.

## II.—EXPERIMENTAL PROCEDURE

The uranium specimens studied had initial grain-sizes of 0.01 and 0.035 mm. and were cold rolled to 4 and 19% reduction in thickness and subsequently annealed for periods ranging from a few minutes to a few hours in the temperature region 400°–650° C.

Specimens were given the usual metallographic preparation and electropolished in one of the solutions recommended by Mott and Haines.<sup>5</sup> The solution most frequently employed was a mixture of two parts sulphuric acid, one part orthophosphoric acid, and two parts water. Microscopical examination was carried out under polarized-light illumination on a Vickers projection microscope.

## III.—GRAIN GROWTH IN METALS

In annealed metals, the energy of the grain boundary is found to be largely independent of the orientation difference between neighbouring grains or of the orientation of the boundary relative to either grain, except in special cases, e.g. when the two grains have a very similar

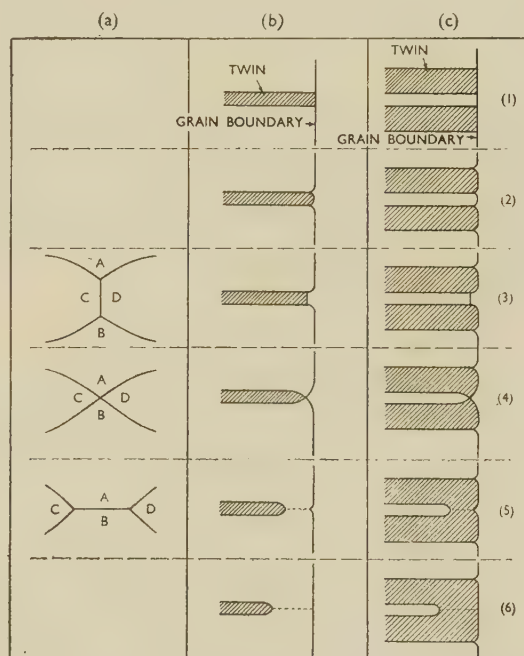


FIG. 1.—Showing Mechanisms for: (a) Grain Growth; (b) Freeing of Twins from Grain Boundary; (c) Joining of Neighbouring Twins at Grain Boundary.

orientation. Boundaries tend to migrate towards their centres of curvature on annealing, since there is more pull on an atom from its neighbours on the concave side; similarly (considered two-dimensionally) grain-boundary intersections become three-rayed, with the included angles tending to approach 120°. Equilibrium is never attained, because adjustments required to bring one area into

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equilibrium will cause disturbances in neighbouring areas. During grain growth, three-sided grains rapidly disappear, grain-face curvature and disequilibrium at intersections combining to make them very unstable. The process by which a grain with four or more sides becomes three-sided seems to be the rate-controlling factor in grain growth. Smith<sup>7</sup> and others have described this stage, which is illustrated in Fig. 1 (a). Here, because of curvature of the boundaries (Fig. 1 (a) (3)), the side separating grains *C* and *D* tends to shorten until it becomes a point (Fig. 1 (a) (4)). This configuration is unstable, and grains *C* and *D* will tend to separate, introducing a boundary between *A* and *B* (Fig. 1 (a) (5)). Fullman<sup>8</sup> and Nielsen<sup>9</sup> have pointed out that if the orientation difference between *A* and *B* is slight or the grain-boundary energy is small for some other reason, the separation of *C* from *D* will proceed much more rapidly. The number of grains is not reduced by this process, but if grains *C* or *D* become three-sided they will then be rapidly absorbed.

Although the assumption is not strictly correct, the surface energy may be regarded as giving rise to a surface tension, and this terminology will be used in the following discussion.

#### IV.—MICROSTRUCTURAL OBSERVATIONS

##### 1. TWIN-BOUNDARY ALTERATIONS

No precise measurements have been made of the interfacial energies of twin boundaries in uranium; these cannot be negligible, however, since on annealing the junctions of twin and grain boundaries tend to migrate down the twin boundaries. This behaviour is very obvious in lightly deformed uranium, and it is present in many of the photomicrographs reproduced (e.g. Figs. 9, Plate XV and 20, Plate XVII).

##### (a) *Freeing of Twins from Grain Boundaries*

Perhaps the most characteristic feature of the microstructure of lightly deformed and annealed uranium is the number of twins which become free of the grain boundary at one or both ends. The mechanism by which this probably occurs is sketched in Fig. 1 (b).

In the as-deformed state the twin intersects the grain boundary without deflecting it appreciably (Fig. 1 (b) (1)). The interfacial tensions will not be in equilibrium and, on annealing, the grain boundary will be pulled down by the twin boundaries (Fig. 1 (b) (2)). If the twin is sufficiently thick, probably little further will happen; but if the twin is thin, considerable curvature will be introduced at the boundary between the twin and the neighbouring grain, and the boundary will migrate towards its centre of curvature (Fig. 1 (b) (3); cf. Fig. 1 (a) (3)). The boundary will then have nothing to balance it and will quickly contract to a point (Fig. 1 (b) (4); cf. Fig. 1 (a) (4)). These junctions will then separate, the twin being absorbed from its end and the grain boundary returning towards its original position (Figs. 1 (b) (5) and (6); cf. Fig. 1 (a) (5)).

No grain was found with twins showing all stages of break-away, but Fig. 5 (Plate XV) illustrates some stages. Twins *A* and *C* have pulled out the grain boundary and are about to break away. At twin *B* this

has occurred, but the grain boundary still shows a projection opposite to it.

If a slight disorientation exists between the two parts of the grain, absorption of the twin should be accompanied by the formation of a boundary between the two parts of the grain (shown dotted in Fig. 1 (b)). No evidence of a disorientation was ever detected microscopically, but examination by polarized light is sensitive only to disorientations greater than  $\sim 2^\circ$ . Cahn<sup>6</sup> observed that the Laue pattern from such a grain was not perfect.

##### (b) *Joining of Twins*

Twins joined over part of their length are another common feature of partially recrystallized uranium. The joining may occur at the grain boundary by a mechanism similar to that of twin break-away (Fig. 1 (c)). Here the requirement is that the twins should be wider than the inter-twin distance. The boundary is pulled in between the twins and then contracts to a point (Fig. 1 (c) (4); cf. Fig. 1 (a) (4)). The two twins are brought into contact, and a boundary spreads up between the twins, while the original grain boundary reverts to its old position. Quite widely spaced twins may be joined if the outer boundaries are stabilized, e.g. by inclusions, other twins, or change in angle of boundary. Fig. 6 (Plate XV) illustrates this occurring at a grain corner where an inclusion is also present.

As in the case of twins coming free, doubt exists as to whether the twins join perfectly or whether a small-angle boundary exists between them.

##### (c) *Grain-Boundary Migration ("Strain-Induced Boundary Migration")*

During both the processes described above, the grain boundary between twins initially migrates into the twinned grain. Whether the twins become free or become joined depends on their thickness compared with the inter-twin distance. If, however, the twin thickness is commensurate with the twin spacing all along the boundary, it is unlikely that either of these processes will predominate, and the grain boundary will then continue to advance into the twinned grain.

This probably occurs quite frequently, but it is difficult to detect metallographically when it takes place uniformly and leaves only a twin-free grain in its wake (Fig. 7, Plate XV). When the grain is more heavily twinned in one portion, the grain boundary may make a local advance in this area, particularly if the grain boundary is locally tethered elsewhere, as by an inclusion. Fig. 8 (Plate XV) illustrates this at three places on the boundary of grain *C*. The three prongs of invading grains have almost met inside the grain and have cut off little islands of the disappearing grain. Such islands are occasionally detected metallographically (*A*, Fig. 9, Plate XV). Grains which are very heavily twinned are likely to be invaded by all their neighbours (Fig. 10, Plate XV) and disappear completely.

This behaviour is similar to the phenomenon of "strain-induced boundary migration" studied in aluminium by Crussard<sup>10</sup> and by Beck and Sperry.<sup>11</sup> The boundaries of lightly deformed coarse-grained aluminium are found to migrate away from their centres of curvature, to become very jagged in appearance, and often to cut off areas of the consumed grain during their advance.



Beck<sup>12</sup> has postulated that there is a greater pull from sub-boundaries in front of the advancing interface, and this hypothesis finds direct experimental proof with uranium.

#### (d) Growth of Twins from Neighbouring Grains

It is sometimes found that a twin from a grain can grow into a neighbouring grain if it abuts on a sufficient number of twins in that grain. Fig. 2 illustrates a simple mechanism by which this can occur, and Fig. 11 (Plate XVI) shows an example. Generally the twin will

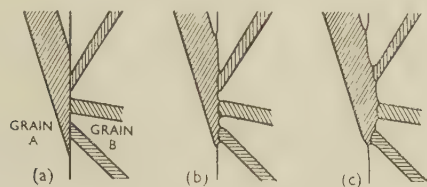


FIG. 2.—Showing Mechanism for Growth of Twin from Grain A into Neighbouring Grain B. (Twins shown shaded.)

grow only a short way into the other grain before the “pulling” twins tend to break away. However, if the grain is very heavily twinned, a twin from an adjacent grain may continue growing. In Fig. 12 (Plate XVI), a twin of A has grown through into a neighbouring grain B, while at the other boundary it has broken loose. With a little more annealing, the twin in A would probably have been absorbed, giving the impression of a nucleus of foreign orientation at the boundary of B.

#### (e) Behaviour of Twin Intersections

During deformation, twins frequently encounter previously formed twins. In such cases they generally taper to a point on the obstructing twin. Deformation may be transferred to the other side of the obstacle by the formation of a secondary twin in the obstacle, or, if the twin is very thin, without any obvious plastic deformation in it. Cahn<sup>6</sup> has shown that in certain circumstances—if the trace of the crossing and secondary twin are parallel in the plane of the crossed twin, and if the direction and magnitude of shear are the same in the crossing and secondary twins—such a transference occurs very easily, the crossing twin impinging on the crossed twin without any narrowing and generating a secondary twin across the area of contact. He analysed the conditions for crossing in  $\alpha$ -uranium and found that they are rigorously obeyed for four types of intersections, and approximately obeyed in a few others. He observed only two of these four types experimentally, namely: (i) (172) crossing (172), (172) crossing ( $\bar{1}\bar{7}2$ ); and (ii) (172) or ( $\bar{1}\bar{7}2$ ) crossing (130), and (172) or (172) crossing (130); these occurred frequently. These intersections have very characteristic configurations, so that the changes they undergo on annealing can be followed metallographically with some degree of certainty.

The commonest type of intersection found by Cahn<sup>6</sup> was type (i) above. Here the crossing twin intersects the crossed twin obliquely without changing direction, as shown schematically in Fig. 3 (a). The four four-ray intersections at the corners of the secondary twin are not in equilibrium under surface forces (Fig. 1 (a) (4) shows

the corresponding stage during grain growth) and, on annealing, new boundaries will be created and bring the crossed and crossing twins into contact at 1 and 3, and the secondary twin and the matrix into contact at 2 and 4, thus causing the secondary twin to become a six-sided grain (Fig. 3 (b)). Fig. 13 (Plate XVI) shows an intersection of type-{172} twins after annealing, where this alteration is apparent. Further annealing will cause more changes which will depend on the relative thickness of the crossed and crossing twins, and on the spacing of the twins in each family. In Fig. 3 (c)–(f) the changes likely to occur when the twins are of comparable thickness and widely spaced have been sketched. Here growth will lead to a spread of the interface between the matrix and the secondary twin (Fig. 3 (c)), until eventually crystallites M and M' of matrix orientation are brought into contact around the secondary twin. Examples corresponding fairly closely to these stages are marked c and e on Fig. 14 (Plate XVI). Further growth will cause the rapid absorption of the secondary twin and, subsequently, of the crossing and crossed twins. If the crossing twin is much thinner than the crossed twin, it is likely to become detached from the crossed and secondary twins quite early in growth. However, the secondary twin, and subsequently the crossed twin, will eventually become absorbed by the matrix grain. If the spacing of either set of twins is comparable to their thickness, this set will probably become joined during growth (cf. at X in Fig. 14), and the secondary twin orientation may also be preserved if the spacings and thickness of both sets are comparable. Generally, however, the secondary twins will disappear unless some of their vertices are stabilized by other twins, grain boundaries, or inclusions. In Fig. 15 (Plate XVI) the secondary twins in the centre of the grain (A, B, C) are

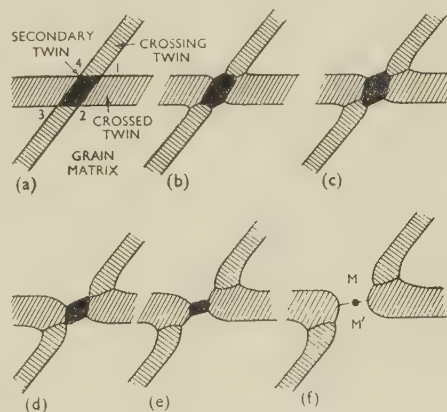


FIG. 3.—Alterations Expected on Annealing Type-(172)-(172) Twin Intersections.

being absorbed, while at the grain boundary (D, E, F) one at least has grown.

A similar analysis shows that the secondary twin in the type-(ii) intersection mentioned above should become a six-sided grain at an early stage of growth, and that the subsequent fate of crystals of orientations of the crossed, crossing, and secondary twins should depend on their relative thicknesses and spacings in the same manner as for the {172}-type of intersection. Very few intersections of this type were observed in the deformed specimens,

and on annealing only the first stage of growth (Fig. 16, Plate XVI) was found.

## 2. KINK-BOUNDARY ALTERATIONS

### (a) *Changes at Grain Boundaries*

The alterations observed on annealing kink bands seem to be confined to changes at their boundaries, unless they contain subsidiary bend planes. Fig. 17 (Plate XVII) shows the intersection of a kink band *A* with a grain boundary after annealing. The junctions of the boundaries have migrated along the kink boundaries, suggesting that these also possess an appreciable surface energy. The energy of the boundary appears to increase with the disorientation across it, and cases have been observed of kink bands with boundaries of strong and weak disorientation where all the alterations on annealing are confined to the strongly disoriented boundary. The energy of the kink boundaries appears to be lower than that of twin boundaries, since considerable alterations were observed in the latter while little change had occurred in the former. It is difficult to find examples of large alterations of kinks that are not caused by the presence of twins, since both are generally present. It

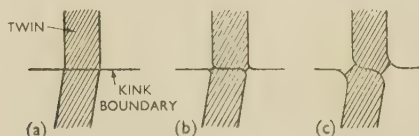


FIG. 4.—Alterations Expected on Annealing at Places Where Twin Crosses a Kink Boundary.

appears, however, that nearly all the alterations found for twins at grain boundaries can occur with kinks. Wide kinks may cause the boundary to migrate into the grain (Fig. 18 (Plate XVII) cf. Fig. 8), or the kink may grow into a neighbouring grain (Fig. 19 (Plate XVII); cf. Fig. 12). In Fig. 20 (Plate XVII), the kink band appears to be coming free from the boundary (cf. Fig. 5).

Kink bands often meet other kink bands inside grains, and on annealing there appears to be an approach towards equilibrium angles at their junctions. Greater changes were not observed at these junctions with the annealing times and temperatures studied.

### (b) *Changes at Twin Boundaries*

The alterations to twins impinging on kink boundaries which are produced by annealing are very similar to those of twins at normal grain boundaries. However, since the kink boundary is a surface of only slight disorientation, twins can generally pass through kink bands with slight alteration of direction at the boundaries. In Fig. 4 the changes to be expected on annealing are sketched, while Fig. 21 (Plate XVII) shows these changes among a family of twins crossing a family of kinks. Changes at the kink boundary may cause the twin to become free or to become joined to a neighbour, and such a configuration of twins and kinks is quite rapidly transformed into an assembly of crystallites with two groups of orientations centred on that of the original grain and twin. If a twin encounters a bend plane within the kink, changes will occur there (*A* and *B*,

Fig. 22, Plate XVII). A small twin can grow to quite large dimensions in a region of complex kinking.

## 3. EFFECT OF INCLUSIONS

Inclusions are known to hinder grain growth, and during recrystallization they behave in the same manner, as the grain boundary tethered by the inclusion *D* in Fig. 8 (Plate XV) indicates. Inclusions are sometimes said to act as centres of recrystallization. In uranium this is hardly the case; no real nuclei were associated with inclusions, although the deformation around many was probably more complex than average, and some of the crystallites produced here by deformation grew. Inclusions may assist in preserving or even enhancing minute components of the texture—e.g. two narrow twins quite widely separated may become joined if their outer boundaries are held by inclusions at the grain boundary—especially as alterations generally start at grain boundaries and these are rich in inclusions. Otherwise, their effect on texture is probably small.

## 4. ANOMALOUS OBSERVATIONS

At the small deformations studied, most of the microstructural observations could be explained by grain-boundary migration taking place to reduce surface area and hence surface energy. At larger deformations, similar processes probably occur, but this is difficult to prove, since the finer scale of the structure and the more complex configurations of twins and kinks makes it almost impossible to recognize the original structure from a photomicrograph of a partially recrystallized specimen. Some technique involving continuous viewing during annealing, e.g. electron-emission microscopy, would be required to prove this point satisfactorily.

The same difficulty is also present with lightly deformed specimens, since areas of more complex deformation occur. This is particularly the case where twins abut on other twins but where the crystallographic conditions are not favourable for the formation of the twin intersections discussed above. Here the two sets of intersecting twins become embedded in each other and their ends become kinked. One or more additional twins are frequently generated at such intersections. On annealing, "nuclei" frequently appear to have grown from these crossings. The nuclei do not possess the orientation of the intersecting twins or that of the matrix, though sometimes the orientation is very similar to one of these. More than one family of orientations may have grown in one grain, and generally the orientations of various members of a family are slightly different. This suggests that true nucleation has not occurred, and that fragments of crystallites formed on deformation at the twin intersections have grown on annealing.

There remain a few observations which cannot be readily explained on the assumption that the changes occur in order to reduce interfacial area, and where other effects are probably present. Sometimes, especially in thin, parallel-sided twins, the boundary migrated into the twin by the formation of narrow bulges. No substructure was observable within the twin to account for this movement.

Occasionally a twin breaking free from a boundary will become almost flat-tipped, but this behaviour is erratic, for others of the same family in the grain will be rounded.



Sometimes when a twinned grain is being consumed by a neighbouring grain, the intersections of the twins with the advancing boundary are very similar to the intersections of annealing twins with a boundary where the surface tension of one face of the twin appears to be negative. Fullman<sup>13</sup> had ascribed this to the inability of the coherent boundaries to move out of their planes without a large increase in energy. It is interesting to note that in these cases the orientations of the consuming and the consumed grains are very close (within  $\sim 5^\circ$ ).

## V.—DISCUSSION AND CONCLUSIONS

Microscopical examination suggests that the boundaries of mechanical twins in uranium possess an appreciable surface energy. This is hardly surprising, since the energy depends very greatly on the perfection of fit at the interface. In face-centred cubic materials, for instance, the energy of coherent interfaces of annealing twins have been measured by Fullman<sup>13,14</sup> and found to be 3–5% of a "normal" grain-boundary energy in the case of copper and 21% in the case of aluminium. Here, the alterations of spacing around this interface do not affect first-nearest-neighbour distances, so that much larger energies are to be expected where there are disturbances of spacing at the interfaces, such as Cahn<sup>6</sup> has shown to exist for twins in uranium. Moreover, most of the boundaries, at higher deformation, cannot be coherent, since their outlines are curvilinear. Even when there is a special orientation relationship between two grains (e.g. an annealing twin), the energy of an incoherent boundary is high ( $\sim 80\%$  of that of a normal grain boundary<sup>14</sup>). Thus, movements of twin boundaries formed on deformation, and of new grains growing amongst twins, would be expected, and are actually found, to follow movements predicted from grain growth. Very few examples of grain boundaries moving in directions opposed to those to be expected from a reduction in surface area have been found, and behaviour dependent on orientation differences between grains is equally rare.

Bend planes also appear to possess an appreciable surface energy. Although this has been postulated to account for recrystallization (e.g. Beck,<sup>12</sup>) it does not appear to have been experimentally verified previously.

These observations probably explain most of the cases which have been reported of mechanical twins swelling or becoming absorbed on annealing in other metals and possibly also in minerals (see reviews by Hall<sup>15</sup> and by Cahn<sup>16</sup>). The disappearance of twins leads directly

to a reduction in surface area; neighbouring twins become joined where they intersect a grain boundary or kink band, and twins swell or become punctured if the matrix or twin contains a network of sub-boundaries. If the atomic misfit along the twin boundary were very low, then behaviour resembling that of annealing twins might be expected.

There is little direct evidence that nucleation from atomic dimensions occurs in uranium. True, grains of orientations different from those of existing twins grow from twin crossings, but these are probably crystallites produced by deformation, although the complexity of the crossings and their small size makes direct confirmation difficult.

In lightly deformed uranium, at least, the question whether a particular crystallite formed by deformation grows or becomes absorbed on annealing is determined by the configuration of its boundaries rather than by its perfection. No general statement can be made about whether a particular crystallite will grow or not except that the larger it is with respect to its neighbours the more likely it is to do so. Thus, grains oriented so that they do not twin or kink under the particular deformation applied might be expected to grow.

## ACKNOWLEDGEMENTS

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# CALCULATION OF THE CONTRIBUTION MADE BY GRAIN-BOUNDARY SLIDING TO TOTAL TENSILE ELONGATION \*

1724

By H. BRUNNER,† Mech. Eng., and Professor N. J. GRANT,‡ Sc.D., MEMBER

## SYNOPSIS

The stresses and displacements caused by a shear interface in a tensile specimen are calculated on the assumption that stress and strain are proportional. Comparison of calculated and measured shear displacements during creep shows satisfactory agreement in the plastic range for high-purity aluminium. An equation is derived which relates shear displacements and elongation in a tensile specimen. This equation permits quantitative evaluation of the contribution of sliding along any particular grain boundary to the total elongation.

## I.—INTRODUCTION

A STUDY of the structural changes occurring during deformation, if conducted quantitatively, should enable the contributions made by the various processes to the overall elongation of the specimen to be established. Furthermore, the overall elongation of the specimen at any time should be accounted for completely by the sum of these contributions. One of the contributing processes is the relative displacement along slip bands and grain boundaries, i.e. essentially shear processes. The movement of line markers suitably placed on a specimen surface can clearly reveal the displacements caused by these shear processes. Other methods of deformation, for example kinking, as is well known, also occur. Under creep conditions of testing, these processes have been analysed thoroughly by Grant *et al.*,<sup>1-3</sup> as well as by McLean<sup>4-7</sup> and others.

The problem dealt with in the present paper was the derivation of an equation which would permit the determination of the contribution of shear along a plane to the total elongation of a tensile specimen; such an equation can be obtained only from considerations of strain energy, and the equation obtained is presented below. The solution given by McLean<sup>4-7</sup> is based on a statistical average, and as such is applicable only to finer-grained materials; it does not give the contribution of shearing along a single plane to the total elongation.

Starr<sup>8</sup> has determined the stresses and strains caused by a crack in pure shear, and found that the width of the crack is not influenced by shear if the shear direction is parallel to the crack. For this reason it is possible to apply his solution for cracks to slip problems, despite the fact that the proper boundary condition, namely, that the crack should not part under the influence of stress, was not imposed. A stress configuration corresponding to tension could be achieved by considering additional boundary conditions. However, the strain energy cannot be found simply by such a superposition. It was therefore decided to derive all equations from first principles.

## II.—DERIVATIONS OF EQUATIONS

The present analysis considers the two-dimensional problem of a shear plane in an infinite plate, i.e. it is assumed in the derivation that the shear plane extends through the thickness of the specimen and is essentially normal to the surface of the specimen, and also that the width of the specimen is such that there is no significant interaction between the shear interface and the edge of the specimen. Furthermore, proportionality of stress and strain is assumed; this holds true in the elastic range and may be a fair approximation in the plastic range. A good outline of the mathematical procedures is given by Timoshenko and Goodier,<sup>9</sup> and as far as possible their nomenclature will be used, viz.:

- $S$  = tensile stress applied to the specimen
- $s$ -axis = axis parallel to  $S$
- $t$ -axis = axis normal to  $S$
- $(2c)$  = length of sheared interface
- $x$ -axis = axis parallel to plane of shearing
- $y$ -axis = axis normal to plane of shearing
- $\beta$  = angle between  $s$ -axis and  $x$ -axis = angle between shear plane and applied tension

The geometrical relationships are shown in Fig. 1. Let  $\xi, \eta$  be elliptical co-ordinates, as in Fig. 2. Then:

$$x + iy = c \cosh (\xi + i\eta) = c \cosh \zeta$$

The boundary conditions imposed are:

(1) At points very far from the sheared plane the stresses are not influenced by this shear plane but solely by the applied tension  $S$ . Mathematically this can be expressed as follows:

For  $z \rightarrow \infty$ :

$$\sigma_x + \sigma_y = S$$

and

$$\sigma_y - \sigma_x + 2i\tau_{xy} = -Se^{-2i\beta}$$

(see Timoshenko and Goodier,<sup>9</sup> p. 201).

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(2) The plane of shear has obstacles only at its ends. In the case of slip, these may be grain boundaries or precipitates. In the case of grain-boundary sliding, these obstacles can be triple points or regions of local curvature of the grain boundaries. Mathematically, this second boundary condition can be expressed as :

$$\tau_{xy} = 0, \text{ for } \xi = 0$$

(3) Because of the cohesion across the plane of shear, no parting takes place across this plane. Mathematically, this can be expressed as  $v(+\eta) = v(-\eta)$ , where  $v$  is the displacement in the  $y$ -direction.

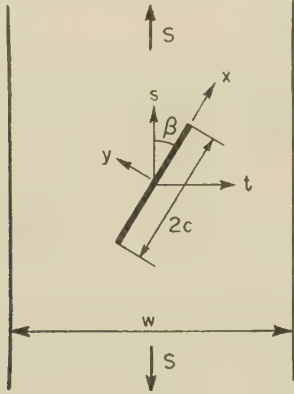


FIG. 1.—Geometrical Relationships and Nomenclature.

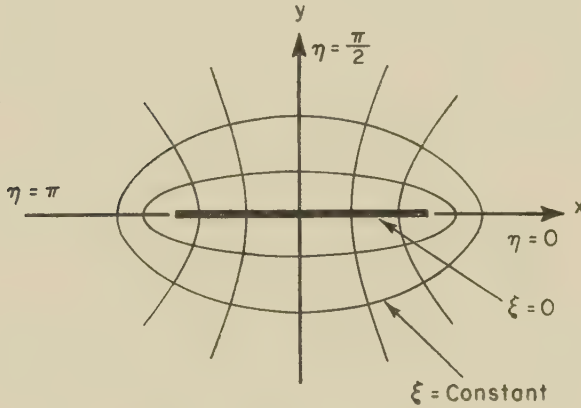


FIG. 2.—Elliptical Co-Ordinates.

(4) Because the geometry of the specimen is essentially skew symmetric, that is, it has two-fold symmetry about an axis perpendicular to the plane of the paper in Fig. 1, stresses and displacements must also be skew symmetric.

The above boundary conditions determine the constants of the general solution. It follows for the complex potentials (stress functions) :

$$\psi(z) = \frac{S \cdot c}{4} (\cosh \zeta - i \sin 2\beta \sinh \zeta) \quad (1)$$

$$\chi(z) = \frac{S \cdot c^2}{8} (-\cos 2\beta \cosh 2\zeta + i \sin 2\beta \sinh 2\zeta) \quad (2)$$

The stresses are given by :

$$\sigma_x + \sigma_y = 4 \operatorname{Re} \psi'(z)$$

$$\text{and} \quad \sigma_x - \sigma_y - 2i\tau_{xy} = 2(z\bar{\psi}''(\bar{z}) + \bar{\chi}''(\bar{z}))$$

From equations (1) and (2) it follows for  $\xi = 0$  (that is, along the plane of shearing) :

$$\text{shear stress : } \tau = 0$$

tensile stress in the  $y$ -direction :

$$\sigma_y = S \sin^2 \beta \quad (3)$$

tensile stress in the  $x$ -direction :

$$\sigma_x = S \left( \cos^2 \beta - \frac{\sin 2\beta}{\sqrt{\left(\frac{x}{c}\right)^2 - 1}} \right) \quad (4)$$

The displacements are given by :

$$u + iv = \frac{1}{2G} [p\psi(z) - z\bar{\psi}'(\bar{z}) - \bar{\chi}'(\bar{z})]$$

where  $u$  = displacement in  $x$ -direction ;

$G$  = shear modulus ;

$$p = \frac{3 - \nu}{1 + \nu} \text{ (for plane stress) and } p = 3 - 4\nu$$

(for plane strain),  $\nu$  being Poisson's ratio.

For the shear plane ( $\xi = 0$ ), it follows that the displacements in the  $y$ -direction are zero ( $v = 0$ ).

The displacements in the  $x$ -direction are (in the case of plane stress) :

$$\frac{u}{c} = \frac{S}{E} \left[ \sqrt{1 - \left(\frac{x}{c}\right)^2} \cdot \sin 2\beta + \frac{x}{c} \frac{1 - \nu + (1 + \nu) \cos 2\beta}{2} \right] \quad (5)$$

The relative displacement  $\Delta u$  across the shear plane is :

$$\frac{\Delta u}{(2c)} = \frac{S}{E} \sqrt{1 - \left(\frac{x}{c}\right)^2} \cdot \sin 2\beta \quad (6)$$

where  $E$  = Young's modulus.

For arbitrary points in the plate, the displacements are :

$$\frac{u_\xi}{h} = \frac{Sc^2}{8G} \left[ \frac{p-1}{2} \sinh 2\xi + \cos 2\beta \sinh 2\xi \cos 2\eta + \sin 2\beta \sinh 2\xi \sin 2\eta \right]$$

$$\frac{u_\eta}{h} = \frac{Sc^2}{8G} \left[ -\frac{p}{2} \sin 2\beta (\cosh 2\xi - \cos 2\eta) + \sin 2\beta \cosh 2\xi \cos 2\eta - \cos 2\beta \cosh 2\xi \sin 2\eta - \frac{1}{2} \sin 2\beta (\cosh 2\xi + \cos 2\eta) - \frac{p-1}{2} \sin 2\eta \right]$$

where  $u_\xi$  = displacement in  $\xi$ -direction ;

$u_\eta$  = displacement in  $\eta$ -direction ;

$$h = \frac{1}{c} \sqrt{\frac{2}{\cosh 2\xi - \cos 2\eta}}$$

The stresses are :

$$\sigma_\xi = \frac{S}{2} \left[ 1 + \frac{\sin 2\beta \sin 2\eta - \sin 2\beta \cosh 2\xi \sin 2\eta}{(\cosh 2\xi - \cos 2\eta)^2} + \frac{\sin 2\beta \cosh 2\xi \sin 2\eta + \cos 2\beta \cosh 2\xi \cos 2\eta - \sin 2\beta \sin 2\eta - \cos 2\beta}{(\cosh 2\xi - \cos 2\eta)} \right]$$

$$\tau_\xi = \frac{S}{2} \left[ \frac{\sin 2\beta \sinh 2\xi \cos 2\eta - \sin 2\beta \sinh 2\xi}{(\cosh 2\xi - \cos 2\eta)^2} + \frac{\sin 2\beta \sinh 2\xi \cos 2\eta - \cos 2\beta \sinh 2\xi \sin 2\eta}{(\cosh 2\xi - \cos 2\eta)} \right]$$



where  $\sigma_\xi$  = normal stress component in  $\xi$  direction;  
 $\tau_{\xi\eta}$  = shear stress in  $\eta$ -direction.

The strain energy  $V$  of the material within the ellipse  $\xi = \text{constant}$  is:<sup>10</sup>

$$V = \frac{1}{2} \int_0^{2\pi} \frac{u_\xi}{h} \sigma_\xi d\eta + \frac{1}{2} \int_0^{2\pi} \frac{u_\eta}{h} \tau_{\xi\eta} d\eta$$

Evaluation of these integrals and expanding  $\xi \rightarrow \infty$  leads to:

$$V = \frac{S^2 c^2 \pi (p+1)}{32G} \cdot (\sinh 2\xi + \sin^2 2\beta) \quad (7)$$

Inserting  $\beta = 0$  in equation (7) yields the strain energy before slip or grain-boundary sliding. The increase of strain energy due to the occurrence of shear is thus:

$$\Delta V = \frac{S^2 c^2 \pi (p+1)}{32G} \cdot \sin^2 2\beta$$

For the case of plane stress:

$$\Delta V = \frac{\pi S^2 c^2}{4E} \cdot \sin^2 2\beta$$

The elongation  $\delta$  of a tensile specimen before shear is increased by an amount  $\Delta\delta$  due to the occurrence of shear. Since it has been assumed that stress and strain are proportional, Castigliano's theorem can be applied in order to find  $\delta$  and  $\Delta\delta$ :

$$\Delta\delta = \frac{\partial \Delta V}{\partial F}$$

where  $F$  is the applied force ( $F = Sw$ ), and  $w$  is the width of the specimen. Thus:

$$\Delta\delta = \frac{\pi S c^2}{2Ew} \cdot \sin^2 2\beta \quad (8)$$

By integrating equation (6):

$$\int_{-c}^{+c} \Delta u dx = \frac{S}{E} 2c \sin 2\beta \int_{-c}^{+c} \sqrt{1 - \left(\frac{x}{c}\right)^2} dx = \frac{S}{E} \pi c^2 \sin 2\beta.$$

Multiplication of both sides by  $\frac{\sin 2\beta}{2w}$  leads to:

$$\frac{\sin 2\beta}{2w} \int_{-c}^{+c} \Delta u dx = \frac{\pi S c^2}{2Ew} \cdot \sin^2 2\beta$$

The right-hand side of this equation and that of equation (8) are identical. Hence:

$$\Delta\delta = \frac{\sin 2\beta}{2w} \int_{-c}^{+c} \Delta u dx \quad (9)$$

Let us now consider a different problem, and assume that the shear interface in Fig. 1 extends to both edges of the specimen (the interface representing, for example, the slip plane of a single crystal). In this case the displacement  $\Delta u$  is constant along the slip plane. Then equation (9) becomes:

$$\Delta\delta = \frac{\sin 2\beta}{2w} \Delta u \frac{w}{\sin \beta} = \Delta u \cos \beta = \Delta u_s \quad (9a)$$

where  $\Delta u_s$  is the vertical component of the displacement  $\Delta u$ . This relationship is almost trivial, but it proves that equation (9) can be applied when the plane of shear extends to all the free surfaces of the specimen. This is the most extreme case of interaction between the shear interface and the specimen edges. It appears safe to assume that equation (9) holds also for an intermediate case, that is, for specimens in which the shear interface extends very nearly to the specimen edges.

Replacing  $x/y$  by  $s/t$  co-ordinates (Fig. 1) in equation (9) leads to:

$$\Delta\delta = \frac{1}{w} \int_{-c'}^{+c'} \Delta u_s dt \quad (10)$$

where  $-c'$  and  $+c'$  are the projections of the triple points on the horizontal axis. However, this step represents a generalization, in as much as  $\beta$ , the angle between the shear plane and the axis of tension, is no longer assumed to be constant. In other words, equation (10) can also be applied to curved grain boundaries along which sliding takes place. Whether this generalization can be justified from a theoretical point of view remains to be proved.

### III.—RESULTS

#### 1. STRESSES

The tensile stress across the sheared plane is constant over the whole length of the sheared plane, and its magnitude is simply equal to the resolved applied tension on this plane (see equation (3)). The normal stress (tension or compression) parallel to the shear plane is "infinite" \* at the end points of the sheared plane. These end points may be precipitates in the case of slip, or triple points in the case of grain-boundary sliding. This severe stress concentration has been pointed out by Chang and Grant<sup>11</sup> (shown schematically in Fig. 14 of their paper). Either cracking or plastic deformation must occur at the triple points.<sup>12</sup> In materials where such plastic deformation is restricted, as for example in aluminium-20% zinc alloys up to 500° F. (260° C.), or 80:20 nickel-chromium alloys at 1200° F. (650° C.), Chang and Grant<sup>11</sup> have, in fact, shown that the triple points are locations of the origin of intercrystalline cavities. However, the foregoing conclusion does not apply to triple points where (as a result of favourable orientation) sliding occurs on two or more sets of adjoining grain boundaries. This is a different problem, which has been considered by Zener.<sup>13</sup>

#### 2. DISPLACEMENTS

The relative displacement across a shear plane, plotted over the shear direction, should be an ellipse (see equation (5)). Fig. 3 shows the measured displacements across a grain boundary of a pure aluminium specimen tested at 500° F. The marker lines (actual spacing = 0.2 mm.) were impressed on the surface before deformation by means of a fine-threaded screw. The agreement with theory appears to be satisfactory. The deviation observed in one end of the curve (that end representing the upper triple point ABC) is due to plastic yielding by fold formation clearly visible in grain A. Fig. 3 shows that for this reason the displacement at the triple

\* The exact value for the stress concentration in the case of slip has been given by Stroh.<sup>16</sup>

point is not zero. Fazan, Sherby, and Dorn<sup>14</sup> and others found that the displacements varied appreciably over a single grain boundary, although the extent and distribution of these variations was not considered or measured.

The maximum relative displacement occurs at the mid-point of the shear plane (i.e. for  $x = 0$ ). For a tensile stress  $S = 100 \text{ lb./in.}^2$ , Young's modulus  $E = 8.5 \times 10^6 \text{ lb./in.}^2$  and a shear plane length ( $2c$ ) = 1 mm.,

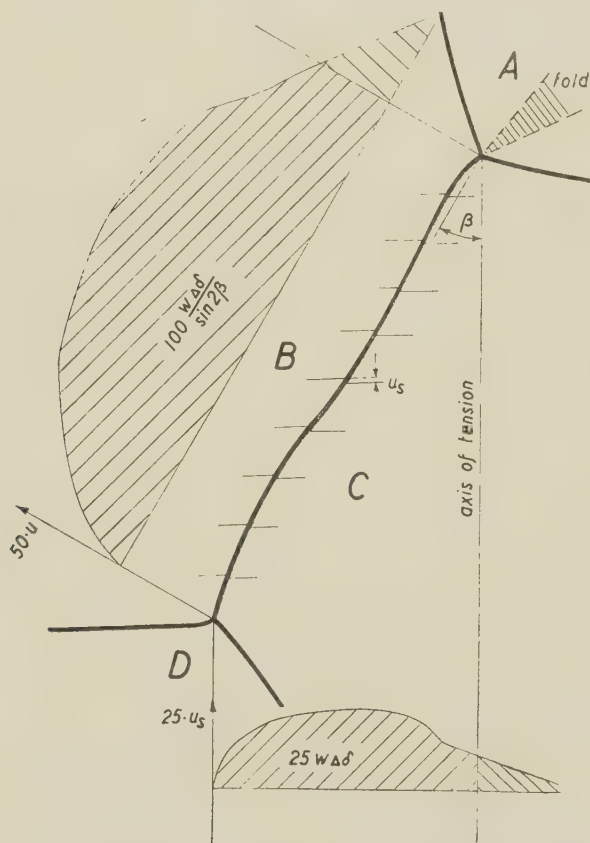


Fig. 3.—Measured Grain-Boundary Sliding and Its Graphical Integration According to Equations (9) and (10).

it follows that the magnitude of the maximum elastic displacement across the shear plane is only  $118 \text{ \AA}$ . A very small amount of slip or grain-boundary sliding is thus sufficient for complete relaxation of the shear stress across a slip plane or grain boundary.

It is interesting to compare the shear displacements obtained by the elementary method applied in this report with those given by the theory of dislocations. Leibfried<sup>15</sup> has studied the equilibrium distribution of dislocations in linear arrays. If the derivative with respect to  $x$  of equation (6) is formed, an equation is obtained which is identical with Leibfried's equation (7).

### 3. ELONGATION

The contribution of grain-boundary sliding along one grain boundary to the total elongation can be calculated

by a graphical integration of the observed displacements according to equation (9) (Fig. 3, upper ellipse), or more easily according to equation (10) (Fig. 3, lower ellipse). Evaluation according to equation (10) has the additional advantage that this equation also considers the displacement component normal to the plane of observation. The contribution of one single slip band to the total elongation could be found by the same methods. If the grain boundary is curved, the method has to be considered as a fair approximation for the time being, that is, until a corresponding study on curved shear interfaces has been made.

The contribution of a fold to the total elongation can also be found by this method (Fig. 3). The practical problem in this case is to achieve sufficient accuracy in measuring the displacement across the fold.

## IV.—SUMMARY

It has been shown that severe stress concentrations occur at the triple points whenever grain-boundary sliding takes place. It was found that the amount of shear displacement plotted over the shear plane is an ellipse. This has been confirmed in the case of grain-boundary sliding by experiment. A very small amount of shear displacement is sufficient for complete relaxation of the shear stresses along the shearing surface. An equation has been derived which permits calculation of the elongation of a tensile specimen caused by sliding along any particular grain boundary.

## ACKNOWLEDGEMENTS

The authors are pleased to acknowledge the important assistance of Dr. A. R. Chaudhuri, and the support of this programme by the Wright Air Development Centre, Aeronautical Research Laboratory.

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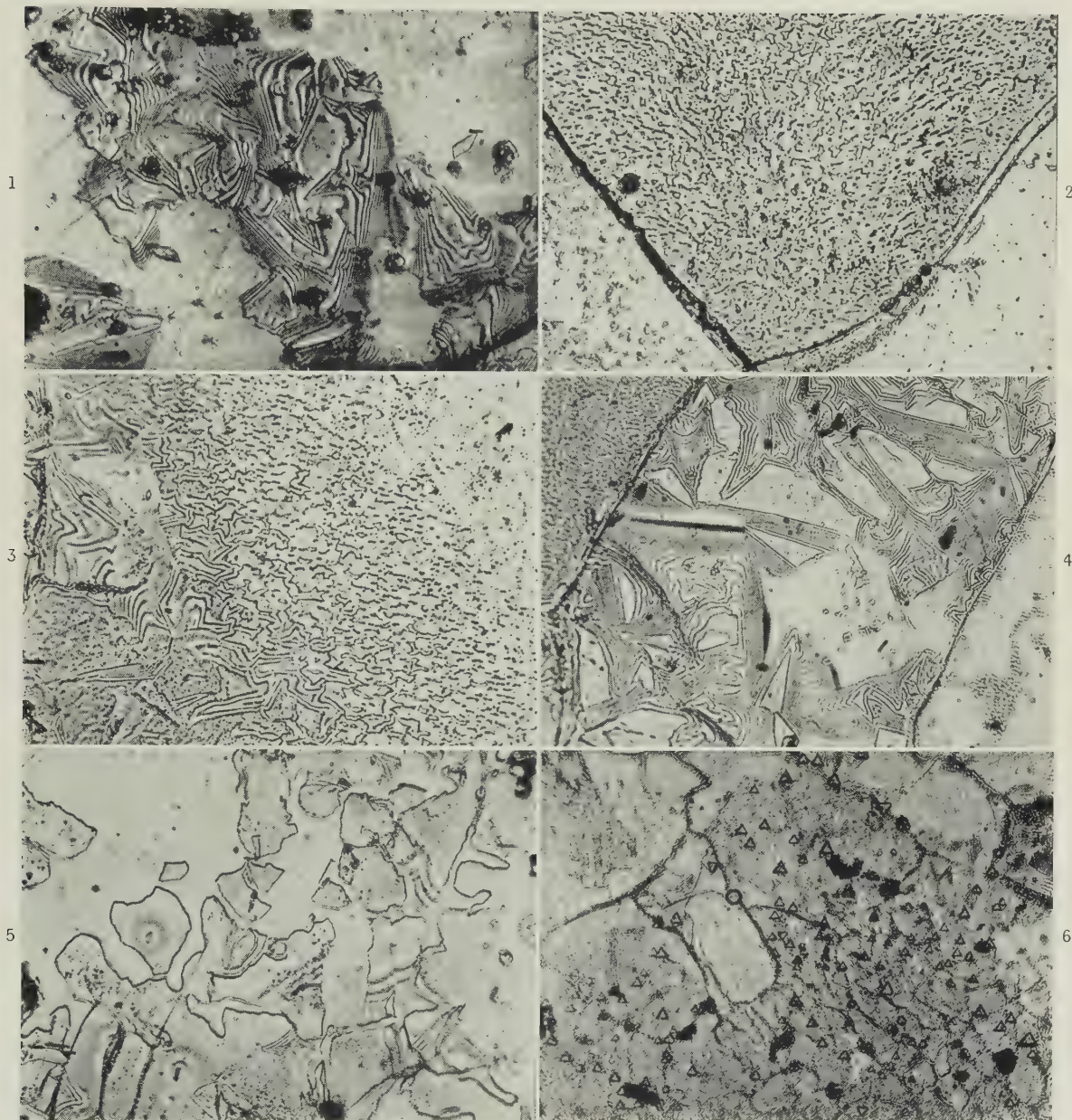


FIG. 1.—A Patch of Partially Detached Oxide, Showing Interference-Fringe Systems.  $\times 850$ .

FIG. 2.—The Early Stages of the Oxide Removal, Showing Initial Sites of Attack.  $\times 470$ .

FIG. 3.—The Expansion and Linking-Up of the Initial Sites of Attack.  $\times 470$ .

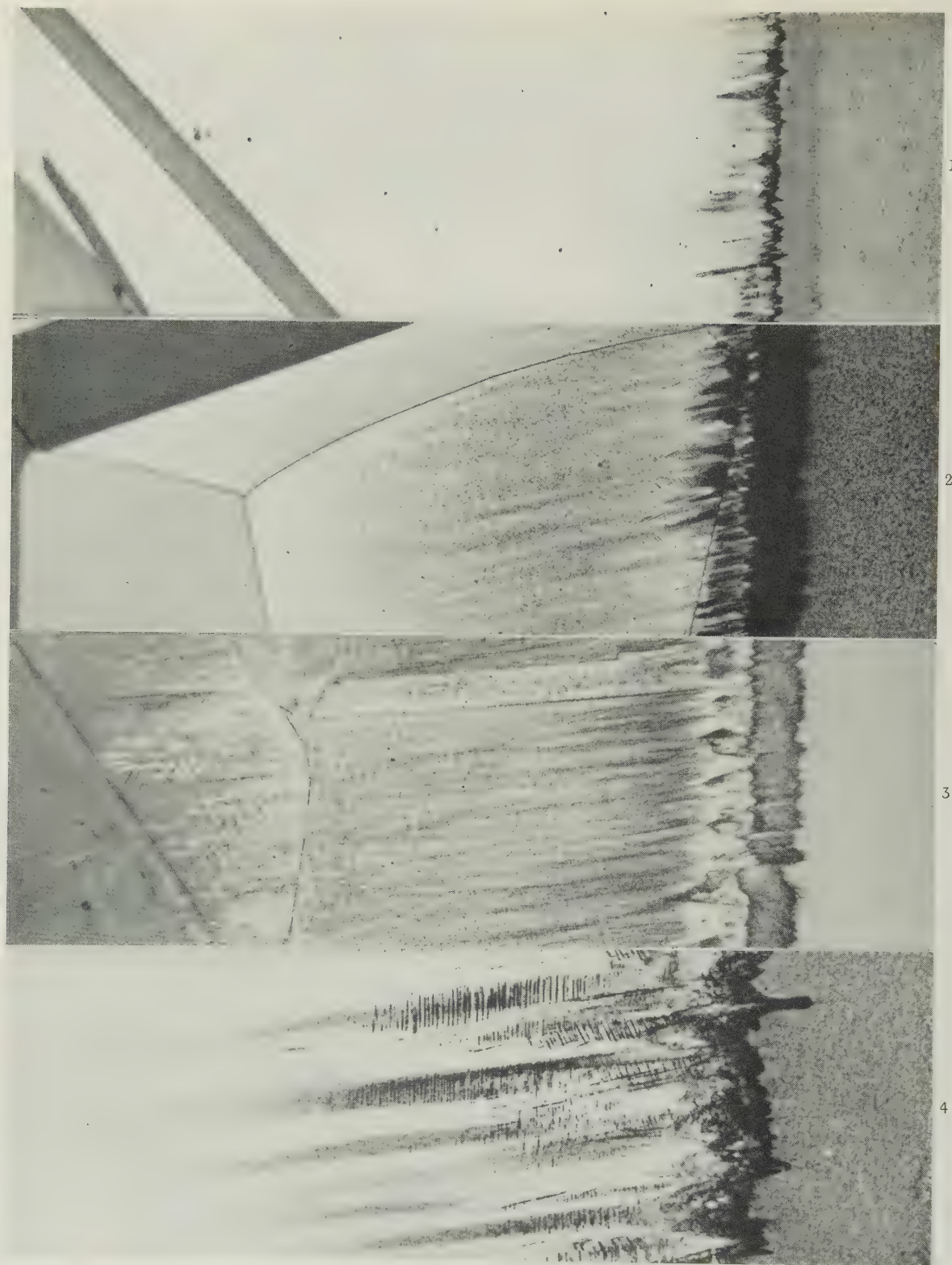
FIG. 4.—An Advanced Stage of the Oxide Removal, Showing the Curling-Up of the Fragmented Oxide Films.  $\times 470$ .

FIG. 5.—Fragmentation of the Oxide Formed at Room Temperature with Little Preliminary Lifting and Buckling.  $\times 470$ .

FIG. 6.—The Triangular Deposits Observed on the Oxide After Immersion in the Flux Containing Cryolite.  $\times 470$ .

(All taken by monochromatic light. Reduced by  $\frac{1}{4}$  in reproduction.)





FIGS. 1-4.—Taper Sections of Brass Surface Abraded on 1/0-Grade Emery Paper at Wear Period 7 (1280 strokes). Taper ratio 8-2.

FIG. 1.—Ferric chloride etch.  $\times 250$ .

FIG. 2.—Low-sensitivity electrolytic thiosulphate etch.  $\times 250$ .

FIG. 3.—High-sensitivity electrolytic thiosulphate etch.  $\times 250$ .

FIG. 4.—Ferric chloride etch.  $\times 1000$ .



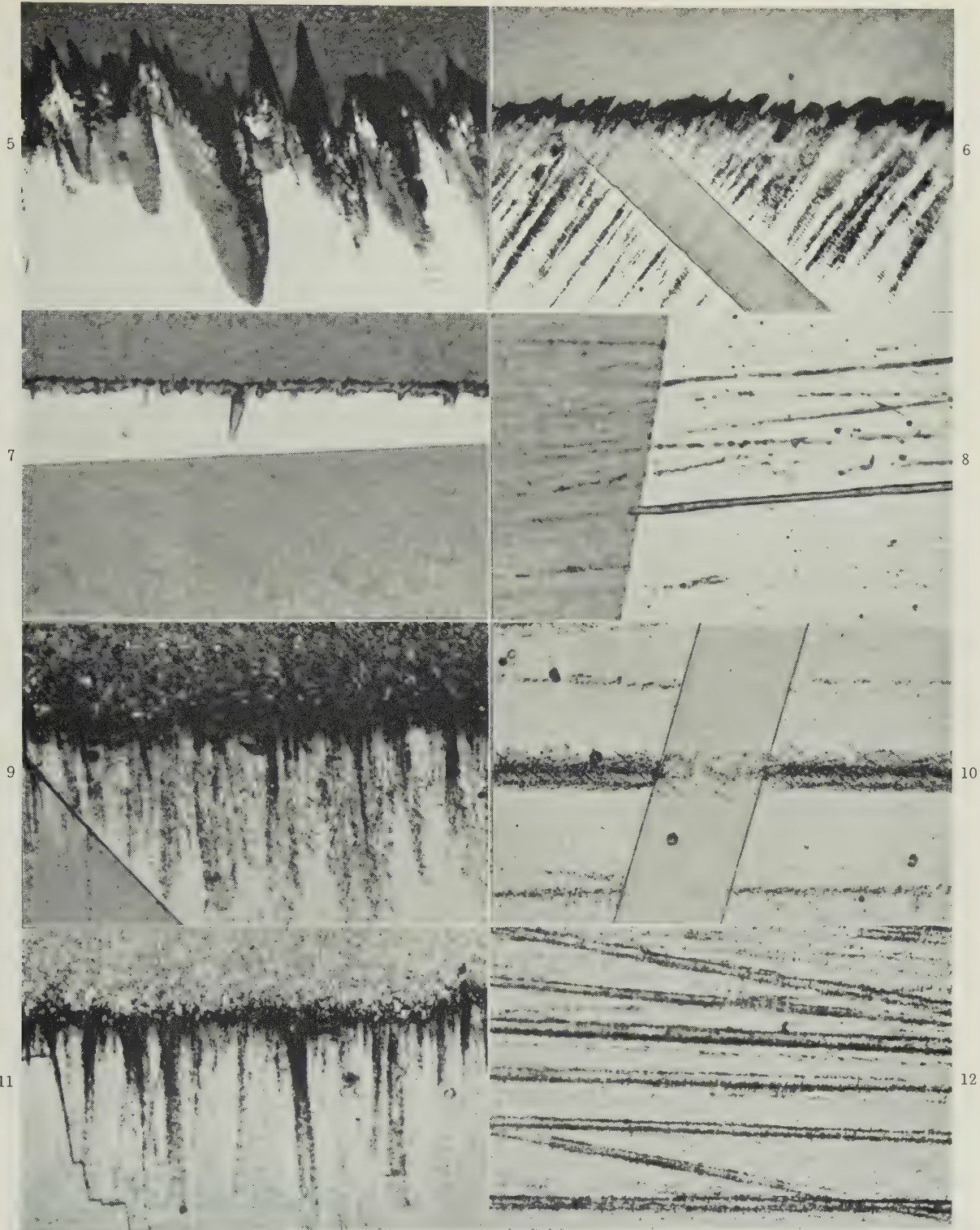


FIG. 5.—Taper Section of Surface Abraded on 1/0-Grade Emery Paper at Wear Period 1 (20 strokes). Ferric chloride etch. Taper ratio 7·7.  $\times 1000$ .

FIG. 6.—Taper Section of Surface Abraded on 2/0-Grade Emery Paper at Wear Period 7 (1280 strokes). Ferric chloride etch. Taper ratio 9·5.  $\times 500$ .

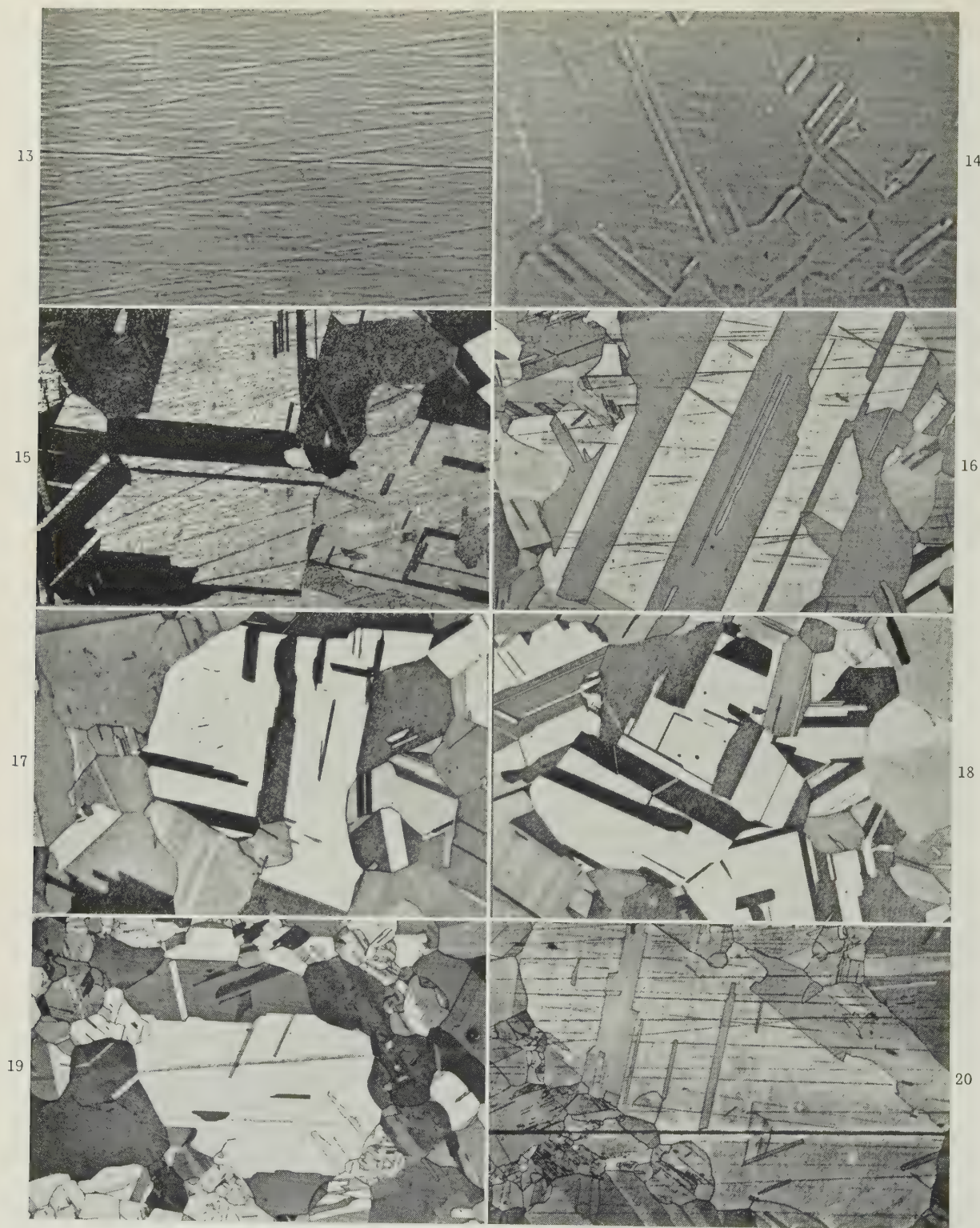
FIGS. 7, 9, and 11.—Taper Sections of Surfaces Polished on a Diamond-Abrasive Pad. Taper ratio 10·9. FIG. 7.—Ferric chloride etch.  $\times 2000$ . FIG. 9.—Low-sensitivity electrolytic thiosulphate etch.  $\times 1000$ . FIG. 11.—High-sensitivity electrolytic thiosulphate etch.  $\times 1000$ .

FIG. 8.—As for Fig. 16.  $\times 2000$ .

FIG. 10.—As for Fig. 19.  $\times 1000$ .

FIG. 12.—As for Fig. 20.  $\times 1000$ .





FIGS. 13-14.—Polished Surfaces, Phase-Contrast Illumination.  $\times 250$ .

FIG. 13.—Polished on (0-1)  $\mu$ -grade diamond pad.

FIG. 14.—As for Fig. 13, then polished for 10 min. on aqueous magnesium oxide paste.

FIGS. 15-18.—Polished Surfaces. Ferric chloride etch.  $\times 250$ .

FIG. 15.—Polished on (0-1)  $\mu$ -grade diamond pad.

FIG. 16.—As for Fig. 15, then polished for 10 min. on aqueous magnesium oxide paste.

FIG. 17.—As for Fig. 15, then polished for 5 min. on magnesium oxide paste containing 8 g./l. ammonium persulphate.

FIG. 18.—As for Fig. 15, then polished for 5 min. on magnesium oxide paste containing 16 g./l. ammonium persulphate.

FIG. 19.—As for Fig. 17, but etched by low-sensitivity electrolytic thiosulphate method.  $\times 250$ .

FIG. 20.—As for Fig. 17, but etched by high-sensitivity electrolytic thiosulphate method.  $\times 250$ .





FIGS. 21-25.—Surfaces of Zinc Polished on (0-1)  $\mu$ -Grade Diamond Abrasive Pad and then for 1 min. on a Magnesium Oxide Paste.

FIG. 21.—Phase-contrast illumination.  $\times 250$ .

FIG. 22.—Same field as Fig. 21, after etching in chromic oxide reagent.  $\times 250$ .

FIG. 23.—Same field as Fig. 21, polarized light.  $\times 250$ .

FIG. 24.—As for Fig. 23, but specimen rotated through  $90^\circ$ .  $\times 250$ .

FIG. 25.—As for Fig. 23.  $\times 2000$ .

FIG. 26.—Debris (70 : 30 Brass) Recovered from Cast Alumina-Wax Lap. Dark-field illumination.  $\times 1000$ .

## PHOTOMICROGRAPHS OF URANIUM-PALLADIUM ALLOYS.

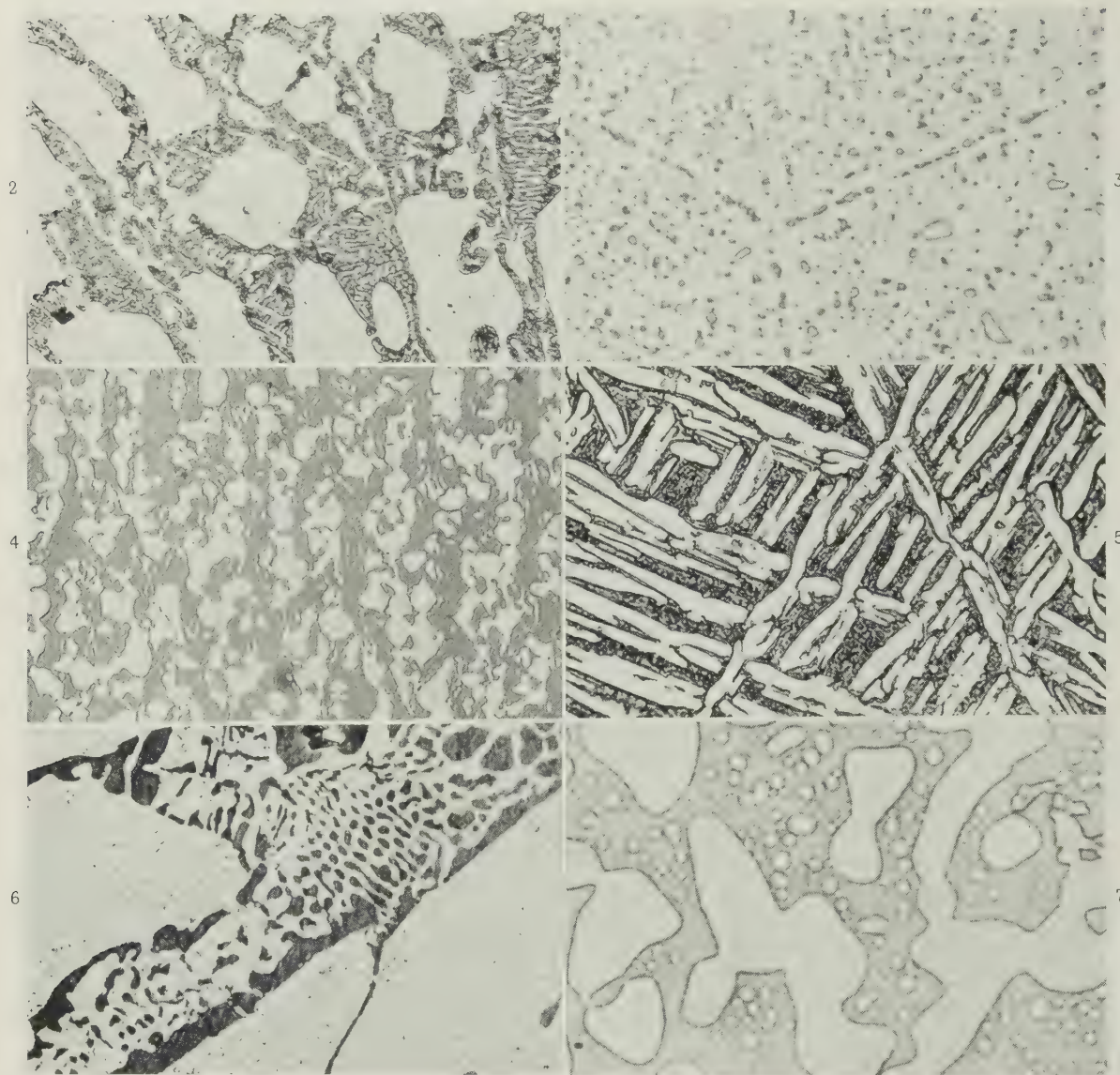


FIG. 2.—10.0 Wt.-% Pd. Slowly cooled in high-frequency furnace. Primary uranium + eutectic. Etched 50%  $\text{HNO}_3$ .  $\times 500$ .

FIG. 3.—2.02 Wt.-% Pd. Annealed for 41 hr. at  $700^\circ\text{C}$ . and quenched, after solution-treatment at  $970^\circ\text{C}$ . Fine precipitate of  $\text{UPd}_3$  in uranium matrix. Etched 50%  $\text{HNO}_3$ .  $\times 2000$ .

FIG. 4.—33.0 Wt.-% Pd. Annealed for 1 month at  $995^\circ\text{C}$ . and quenched.  $\text{UPd}$  (half-tone) +  $\text{U}_5\text{Pd}_6$ . Etched 50%  $\text{HNO}_3$ .  $\times 150$ .

FIG. 5.—24.0 Wt.-% Pd. Rapidly cooled in arc furnace. Primary  $\text{UPd}$  needles + fine eutectic. Etched  $\text{HNO}_3 + \text{HCl}$ .  $\times 500$ .

FIG. 6.—28.0 Wt.-% Pd. Slowly cooled in high-frequency furnace. Primary decomposed  $\text{UPd}$  + eutectic. Etched in steam.  $\times 500$ .

FIG. 7.—20.9 Wt.-% Pd. Annealed for 6 weeks at  $980^\circ\text{C}$ . Uranium (white) +  $\text{UPd}$  (half-tone). Unetched.  $\times 150$ .



## PHOTOMICROGRAPHS OF URANIUM-PALLADIUM ALLOYS.

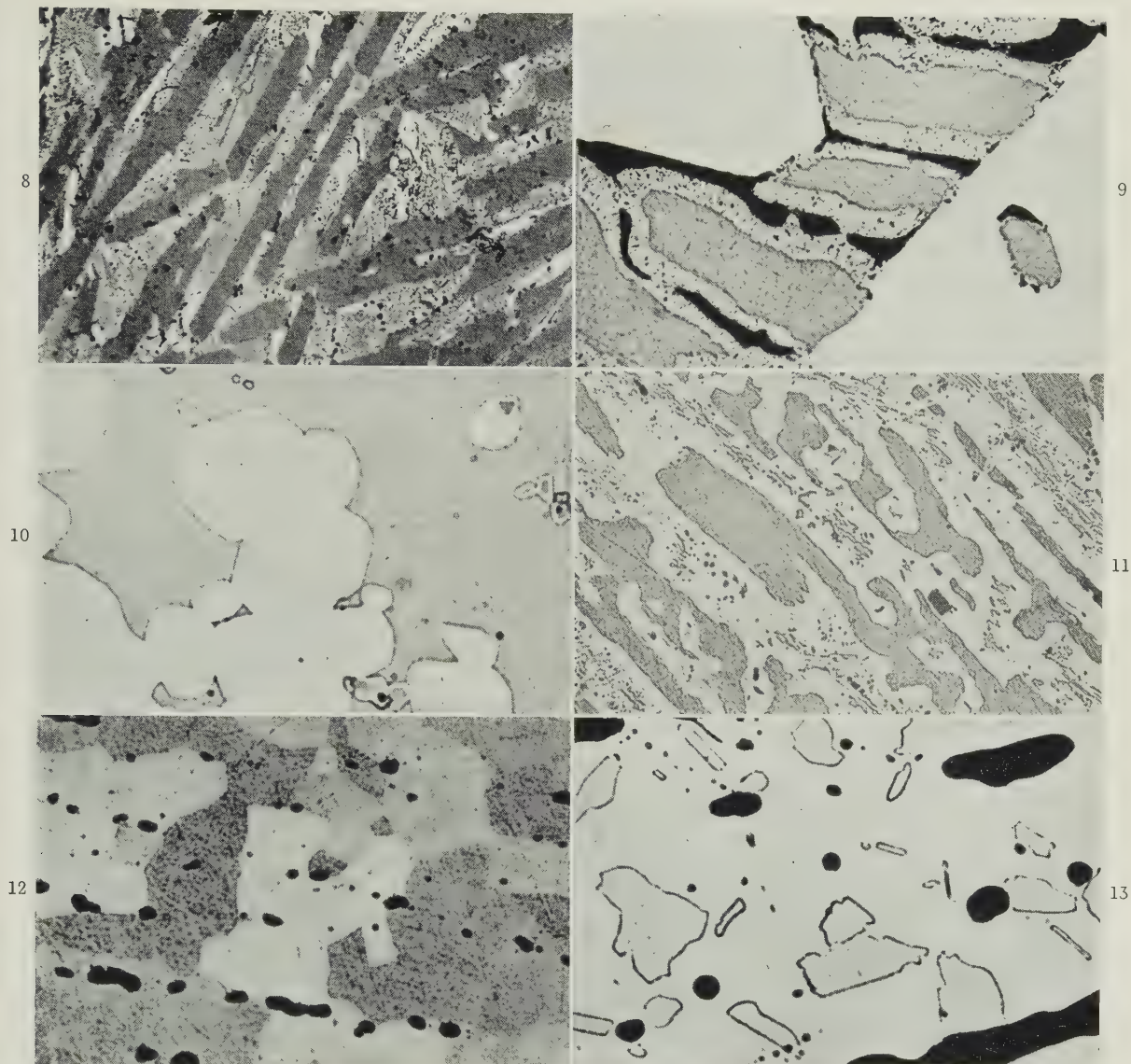


FIG. 8.—32.0 Wt.-% Pd. Slowly cooled in high-frequency furnace. Primary  $U_5Pd_6$  surrounded by UPd (decomposed). Etched 50%  $HNO_3$ .  $\times 250$ .

FIG. 9.—50.2 Wt.-% Pd. Slowly cooled in high-frequency furnace. Primary  $UPd_3$  (white) +  $U_5Pd_6$  (half-tone) + UPd (decomposed) + U (black). Etched 50%  $HNO_3$ .  $\times 500$ .

FIG. 10.—38.0 Wt.-% Pd. Annealed for 29 days at  $1010^\circ C$ . and quenched.  $UPd_3$  (white) +  $U_5Pd_6$  (half-tone) + unsoundness. Unetched.  $\times 150$ .

FIG. 11.—61.6 Wt.-% Pd. Slowly cooled in high-frequency furnace.  $UPd_3$  (half-tone) +  $\delta$  (white). Etched 20%  $HNO_3$  + 10%  $HCl$ .  $\times 150$ .

FIG. 12.—64.0 Wt.-% Pd. Annealed for 1 hr. at  $1425^\circ C$ . and quenched.  $\delta$  + unsoundness. Etched 20% potassium cyanide + 20% ammonium persulphate.  $\times 150$ .

FIG. 13.—61.6 Wt.-% Pd. Annealed for 1 hr. at  $1425^\circ C$ . and quenched.  $\delta$  (white matrix) +  $UPd_3$  (half-tone) + unsoundness. Etched 20%  $HNO_3$  + 10%  $HCl$ .  $\times 150$ .

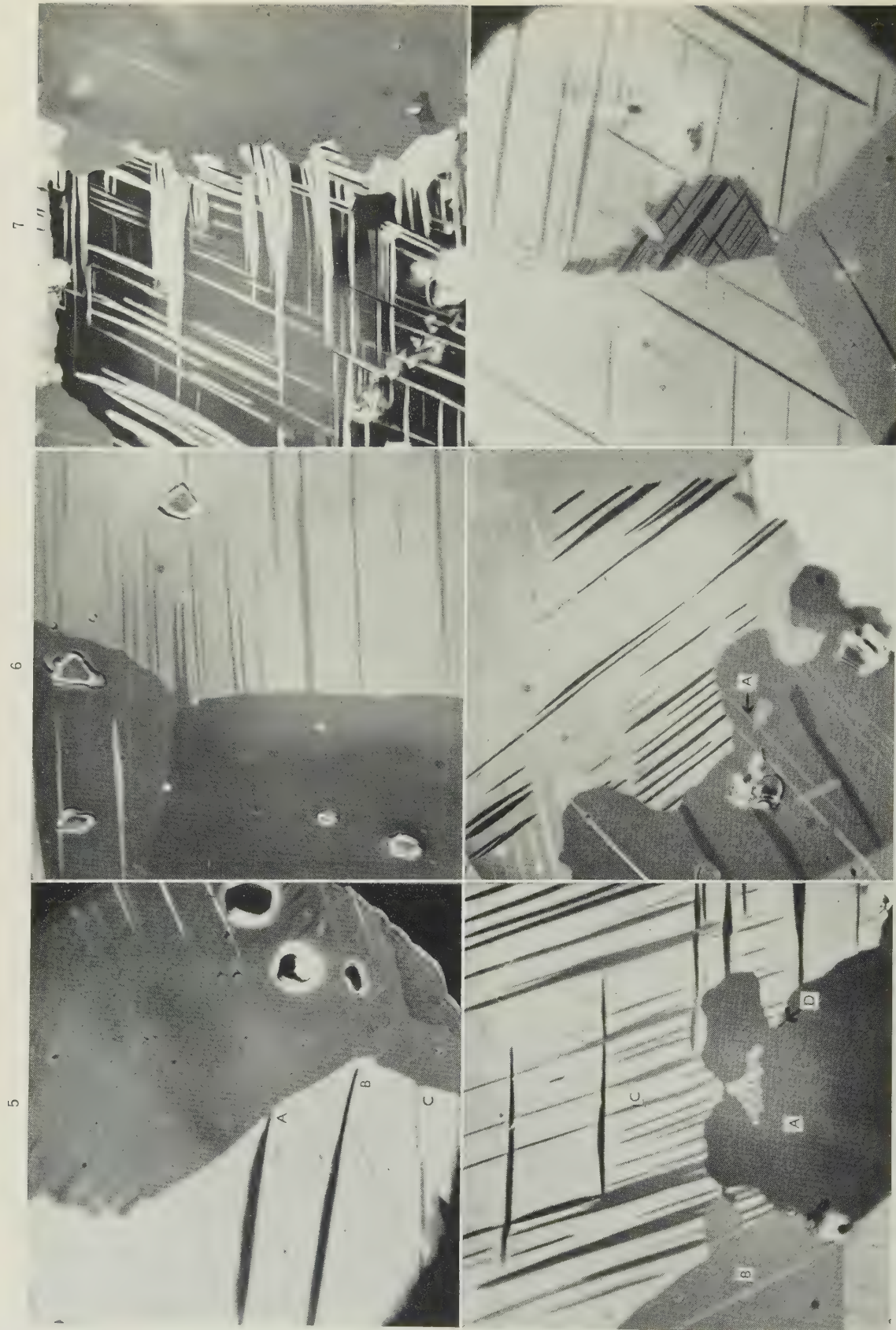
PHOTOMICROGRAPHS ILLUSTRATING BOUNDARY PHENOMENA IN RECRYSTALLIZED URANIUM.  $\times 1200$ .

FIG. 5.—Stages in Freeing of Twins from Grain Boundary on Annealing.

FIG. 6.—Twins Joining on Annealing.

FIG. 7.—Strain-Induced Boundary Migration.

FIG. 8.—Boundary Growing into Grain C at Three Different Places. D is an inclusion.

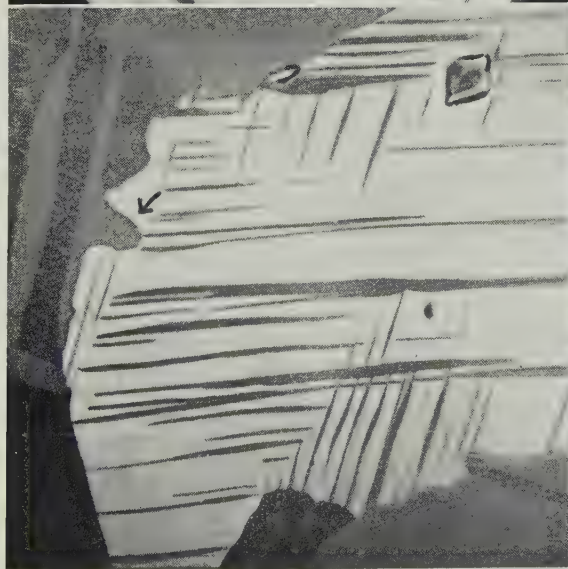
FIG. 9.—Island (I) of Disappearing Grain Left Inside Growing Grain.

FIG. 10.—Heavily Twinned Grain Being Consumed by Its Neighbours.

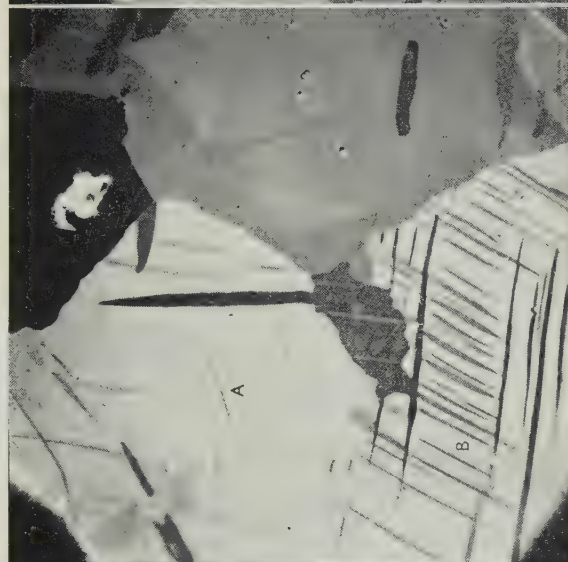
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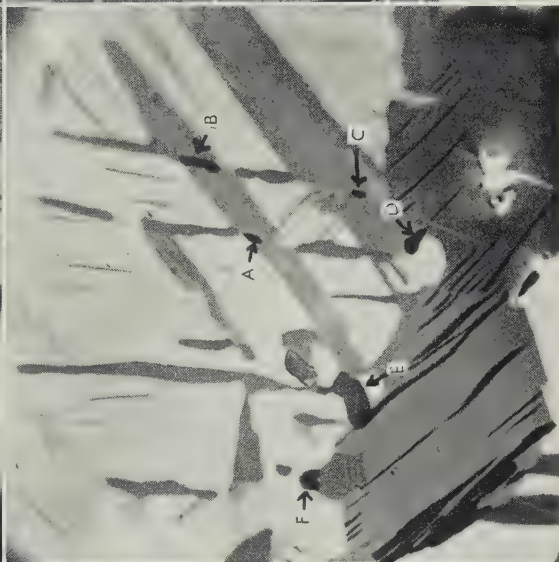
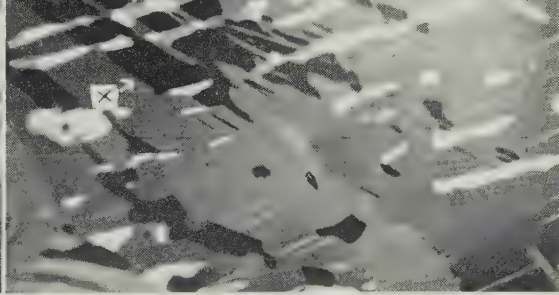
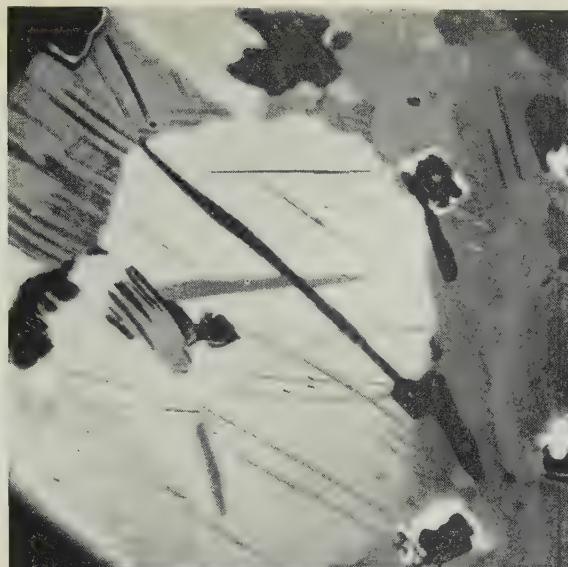
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12



13



14

15

16

FIG. 11.—Growth of Twin into Neighbouring Grain.

FIG. 14.—Alterations on Annealing a Group of {172} Twins.

FIG. 15.—Alterations on Annealing a Group of {172} Twins, Illustrating Fate of Secondary Twins (lettered, see text).

FIG. 16.—First Stage of Growth of Type-(172)-(130) Twin Intersection.

FIG. 12.—Absorption of Twin in Grain A While Growing into Grain B.

FIG. 13.—Alterations of Type-{172} Twins. *e* and *e* correspond approximately to stages illustrated in Fig. 3 (*c*) and (*e*). *x* indicates joining of closely spaced twins.(All taken by polarized light. Reduced by  $\frac{1}{10}$  in reproduction.)

17



18



19



20



21



22

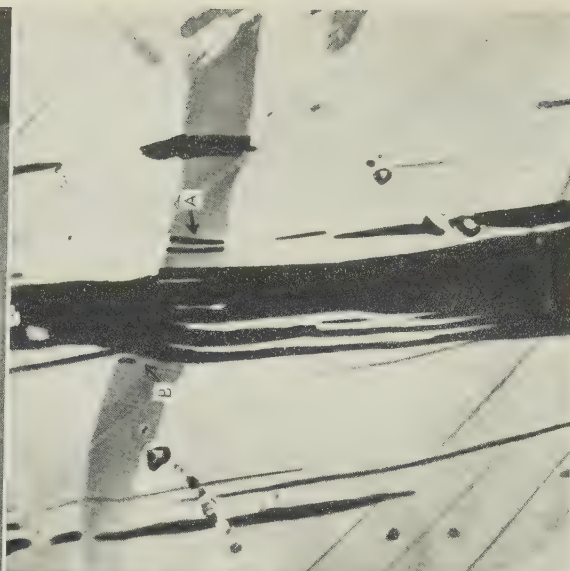


FIG. 17.—Movement of Intersections of Kinks and Grain Boundaries Along Boundaries of Kink (A) on Annealing.

FIG. 18.—Migration of Grain Boundary into Grain Along Kink.

FIG. 19.—Growth of Kink (A) into Neighbouring Heavily Twinned Grain.

FIG. 20.—Kink (A) in Process of Breaking Away from Boundary.

FIG. 21.—Alterations to a Family of Twins Crossing a Group of Kink Bands on Annealing.

FIG. 22.—Alterations to Twins Occurring Along Bend Planes (A and B) in Kink.

(All taken by polarized light. Reduced by  $\frac{1}{16}$  in reproduction.)



# THE EFFECTS OF INTERNAL OXIDATION ON THE TENSILE PROPERTIES OF SOME SILVER ALLOYS AT ROOM AND ELEVATED TEMPERATURES\*

1725

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## SYNOPSIS

The conditions affecting the production of non-metallic phases by internal oxidation of silver alloys containing silicon or aluminium have been investigated. A very marked inhibition of grain growth and recrystallization by the disperse phase was obtained.

Short-time tensile tests at 18°, 200°, 340°, 410°, and 590° C. on silver-0.13% silicon, silver-0.05% aluminium, and silver-0.25% aluminium alloys showed a considerable improvement in strength after internal oxidation. The strength was dependent on the degree of dispersion of the oxide, the greatest improvement being noted in specimens containing the finest dispersion.

## I.—INTRODUCTION

MUCH work has been published on the strengthening of metals by age-hardening, but the increase in strength obtained in this way is destroyed by heating to temperatures above the most favourable ageing temperature, owing to coarsening and solution of the precipitate. Disperse phases that are stable at temperatures below that of their formation can, however, be produced by the internal oxidation of alloys consisting of a noble metal and a small amount of an element having a high affinity for oxygen.

A review of the literature on internal oxidation was given by Cupp<sup>1</sup> in 1953, since then further work has been carried out on the mechanical properties of internally oxidized materials. In the high-temperature field de Jong<sup>2</sup> reported the high creep-resistance of oxidized copper-beryllium alloys, and in a recent paper Martin and Smith,<sup>3</sup> dealing with work carried out subsequent to that presented here, described the creep properties of some internally oxidized copper alloys.

The present paper shows the marked effect of certain disperse phases on the resistance to plastic deformation at room and elevated temperatures, as revealed by short-time tensile tests.

## II.—EXPERIMENTAL

### 1. CHOICE AND PREPARATION OF ALLOYS

The conditions for the formation of a stable dispersion of  $BX$  in a metal  $A$ , by diffusing element  $X$  into a solid solution  $A + B$ , have been discussed by Meijering and Druyvesteyn.<sup>4</sup> They are as follows:

- (i)  $X$  must diffuse more rapidly in solvent  $A$  than does solute  $B$ ; otherwise a surface layer  $BX$  will be formed.
- (ii) The free energy of formation of the compound  $BX$  must be much more negative than that of compound  $AX$ .

When gases are soluble in metals, they generally diffuse far more quickly than do metallic solute elements, and therefore they are ideally suited to the formation of a

disperse phase by this method. In general, noble metals alloyed with a small percentage of a metal having a high affinity for oxygen are very suitable for internal oxidation.

Silver was chosen as the solvent metal in this investigation, since silver oxide is unstable above 200° C., and thus any effect of an external oxide scale on the results of tensile tests at elevated temperatures was eliminated. Aluminium and silicon were selected as solute metals, the former because of the high stability of its oxide and the latter because the disperse phase could be clearly observed under the microscope.

Most of the work described was carried out on silver-0.13% silicon, silver-0.25% aluminium, and silver-0.05% aluminium alloys.

The materials were prepared, by high-frequency melting under a reducing flame, from 99.99% pure silver and spectroscopically pure silicon and aluminium. The ingots were rolled, swaged, and drawn to 20 S.W.G. wire without intermediate annealing. Chemical analyses were carried out subsequently on each alloy.

All the material was given a standard vacuum-annealing treatment in order to obtain a stable and reproducible grain-size before oxidation. For annealing, the silver-silicon alloys were sealed in silica tubes under a vacuum of about  $5 \mu$ , while the silver-aluminium alloys were annealed in continuously evacuated, fused alumina tubes. It was found that if the silver-aluminium alloys were heated in silica tubes the aluminium reduced some silica and oxidation occurred in the surface grain boundaries of the alloy (Fig. 11, Plate XVIII). Figs. 1 and 2 show microhardness traverses of silver-0.25% aluminium specimens oxidized after vacuum-annealing in alumina and silica tubes. There was little hardening near the surface of the material which had been previously annealed in a silica tube, as the surface aluminium had been removed to form massive alumina in the grain boundaries.

For reasons outlined in Section III, the standard oxidizing treatment adopted was heating for 20 hr. in dry oxygen at 650° C. All oxidation treatments were

\* Manuscript received 13 February 1956.

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<sup>‡</sup> Department of Metallurgy, University of Cambridge.

carried out on specimens held in alumina supports designed to ensure free access of oxygen to all surfaces. In cases where oxidation produced marked brittleness, the specimens were bent to the shape of the grips before this treatment.

## 2. METALLOGRAPHY

A convenient method of preparing specimens for microscopical examination was to relief-polish with "Silvo"

to within  $\pm 0.5^\circ \text{C}$ . by means of an electronic proportional controller.<sup>6</sup>

Special friction grips for wires (Fig. 3) were designed and machined from Nimonic 80A.

The extension during testing occurred on a reasonably well-defined gauge-length of 2 in., and there was no measurable contribution due to the grips themselves. Owing to the deflection of the load-measuring spring beam during the course of the tensile tests, the slope of

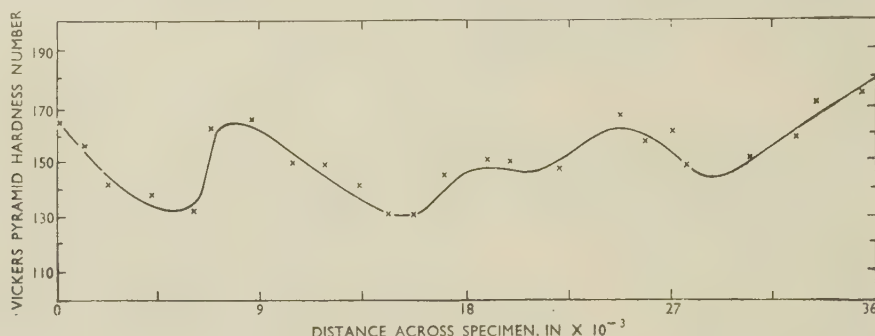


FIG. 1.—Microhardness Traverse of an Oxidized Silver-0.25% Aluminium Alloy After Annealing in an Alumina Tube.

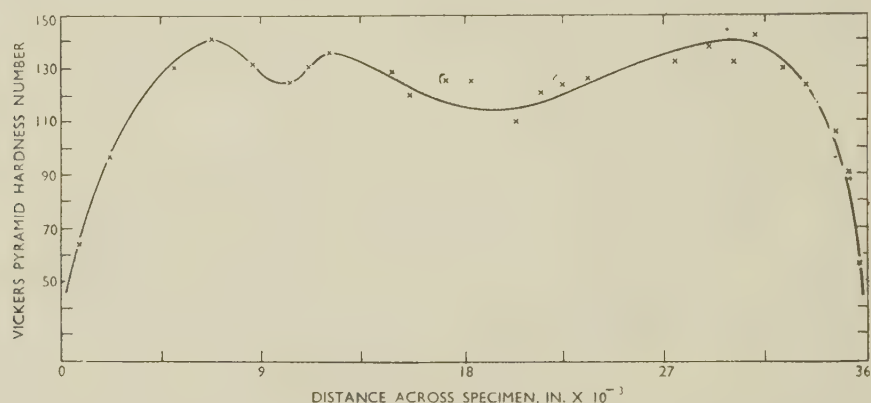


FIG. 2.—Microhardness Traverse of an Oxidized Silver-0.25% Aluminium Alloy After Annealing in a Silica Tube.

to which a small quantity of an ammonia-hydrogen peroxide etching reagent had been added.

Wherever possible, metallographic specimens were prepared by hand-polishing, but in certain instances, such as the preparation of specimens for microhardness measurements, it was essential to remove all the distorted metal from the surface layers, and in these cases electropolishing was used.

The mounting technique adopted for wire specimens requiring an electropolish has been described elsewhere.<sup>5</sup>

## 3. TESTING EQUIPMENT

A "K"-type tensometer modified to take a high-temperature furnace was used for the tests. It was fitted with motor attachments which enabled a range of constant speeds to be obtained and the load/elongation curves were recorded photographically on a rotating drum. A constant strain-rate was employed for each group of tests. The furnace temperature was controlled

the elastic parts of the tensile curves obtained are not a true measure of the elastic moduli of the specimens.

All tests on both vacuum-annealed and oxidized specimens were carried out in an argon atmosphere.

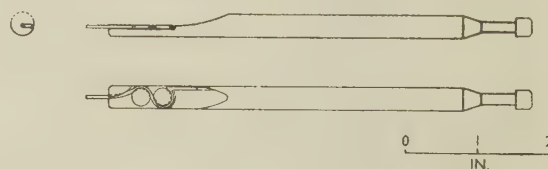


FIG. 3.—Wire Grips for Use at High Temperatures.

## III.—FACTORS AFFECTING THE FORMATION OF THE DISPERSE PHASE

Rhines<sup>7</sup> and Meijering and Druyvesteyn<sup>4</sup> have outlined certain factors affecting the size and distribution of the disperse phase. Many of these have been inves-



tigated in the present work, and attention has been drawn to the importance of others.

A large difference between the free energy of formation of the oxide of the solute and the oxide of the solvent favours the formation of small particles. Thus, the particles formed on the oxidation of silver-aluminium alloys are far smaller than those obtained in silver-silicon alloys, which, in turn, are smaller than those formed in copper-silicon alloys under the same conditions.

The particle size is affected by the rate of diffusion of the solute metal outwards relative to that of the oxygen inwards. When the two rates are equal, either an external scale or a continuous inner oxide film is formed, and when the oxygen diffuses only slightly faster than the solute, the resulting particles are large. Factors which alter the difference between these diffusion rates will change the size of the particles and the tendency to form continuous films.

For silver alloys, it was found that increasing the temperature of oxidation—other factors being constant—increased the average particle size and the tendency to form inner oxide films. Increasing the concentration of the solute had a similar effect.

The importance of some of the above variables was shown by preliminary experiments on a silver-0.13% silicon alloy. This was vacuum-annealed at 900° C. to obtain a large stable grain-size, and specimens were oxidized in air at 650°, 750°, and 850° C. Oxidation at 650° C. led to the production throughout of a disperse phase, but at 850° C. an inner oxide film was formed very close to the surface, which was of the same type as that described by Meijering and Druyvesteyn<sup>4</sup> for alloys containing a high percentage of aluminium or magnesium. When the oxidation was carried out at 750° C., the inner oxide film was still present, though in this case it was situated close to the centre of the wire. Material which had been vacuum-annealed at 675° C. could not be oxidized throughout at 650° C. in air owing to the formation of an inner oxide film. This may have been due to a faster diffusion of silicon along the grain boundaries compared with bulk diffusion through the grains, the fine-grained material thus enabling the silicon to diffuse outwards more quickly and favouring the formation of continuous films.

Increasing the oxygen partial pressure over silver alloys increased the concentration gradient of oxygen, decreased the particle size, and reduced the probability of forming continuous films. Thus, the fine-grained and coarse-grained materials were both oxidized throughout at all temperatures between 650° and 850° C. by heating in oxygen.

During oxidation, the rate of penetration of oxygen decreases as the oxidation front advances, and if the diffusion rate of the solute remains constant, the particle size should increase with distance from the surface. A microhardness traverse from the surface to the centre should thus show a decrease in hardness. Such a traverse across a silver-0.25% aluminium alloy oxidized at 650° C. is reproduced in Fig. 1. The hardness at the surface is greater than that at the centre, but there is also a region of higher hardness between the centre and the outside.

A complete explanation of such effects must take into account the overall rate of movement of the oxidation front and how this is influenced by changes in (a) the

rate of oxygen penetration with depth, and (b) the rate of migration of solute as influenced by changes in concentration gradient as oxidation occurs.

#### IV.—THE INHIBITION OF GRAIN GROWTH

The effect of a disperse phase in preventing grain growth has been discussed by several authors, and has been shown in internally oxidized silver alloys by Chaston.<sup>8</sup> It has been reported by C. S. Smith,<sup>9</sup> from the work of Zener, that an inclusion of low dihedral angle will tend to become attached to the grain boundary and, if it is rigid and insoluble, will tend to anchor the boundary locally. Treating the problem semi-quantitatively, Zener has derived the following formula for the idealized case of spherical particles of equal size and uniform distribution:

$$\frac{R}{r} = \frac{4}{3f}$$

where  $R$  is the radius of curvature of the grain boundary,  $f$  is the fraction of the total volume occupied by the particles, and  $r$  is the radius of the particles.

Fig. 12 (Plate XVIII) shows the grain-size obtained on vacuum-annealing a silver-0.13% silicon alloy in a sealed tube at 675° C. for 20 hr., and the very large grain-size developed in an unoxidized specimen vacuum-annealed at 920° C. for 20 hr. is shown in Fig. 13 (Plate XVIII). Fig. 14 (Plate XVIII) shows the effect of oxidizing the specimen of Fig. 12 at 650° C. in oxygen for 20 hr. and then reheating in air at 920° C. for 20 hr. The average grain diameter increased only slightly, to approximately 0.045 mm., and the outline of the grains became irregular. Any tendency to grain growth, on account of the increase in temperature was hindered by the oxide particles. Under these conditions, it is probable that the grain-size was limited by the size of the particles, and an application of the above formula gave an average value for the radius of the particles of 0.2  $\mu$ . Whilst particles from the material in this condition have not been extracted and examined with the electron microscope, optical micrographs indicate that the above value is of the right order of magnitude.

In addition to the inhibitive effect on grain growth, it has been found that the oxide particles can also markedly inhibit recrystallization.<sup>5</sup>

A single crystal of silver-0.25% aluminium was oxidized throughout at 850° C., cold rolled, and then heated in oxygen at 800° C. for 20 hr. There were no visible signs of recrystallization. A further heating for  $\frac{1}{2}$  hr. at 930° C. in oxygen caused recrystallization to start, but the grains after annealing for 20 hr. were still only very small and non-equiaxed (Fig. 15, Plate XVIII); the Zener formula indicated that the radius of the oxide particles was about 150 Å.

#### V.—TENSILE PROPERTIES

##### 1. SILVER-0.13% SILICON ALLOY

The material was prepared as described in Section II in the following three conditions:

(1) Vacuum-annealed at 675° C.; vacuum-annealed at 650° C.

(2) Vacuum-annealed at 675° C.; oxidized at 650° C.; vacuum-annealed at 850° C.

(3) Vacuum-annealed at 675° C.; oxidized at 650° C.

Fig. 4 gives the load/elongation curves obtained at 18°, 340°, 410°, and 590° C., using a linear strain-rate of 1.35 mm./sec. In each case curves 1 and 3 show clearly

illustrating the stability of the disperse phase at temperatures below the oxidation temperature. The percentage elongation was decreased by internal oxidation, and the specimens tended to fail in an intercrystalline manner even at low temperatures. It is not known whether this brittleness is due to an increased concentra-

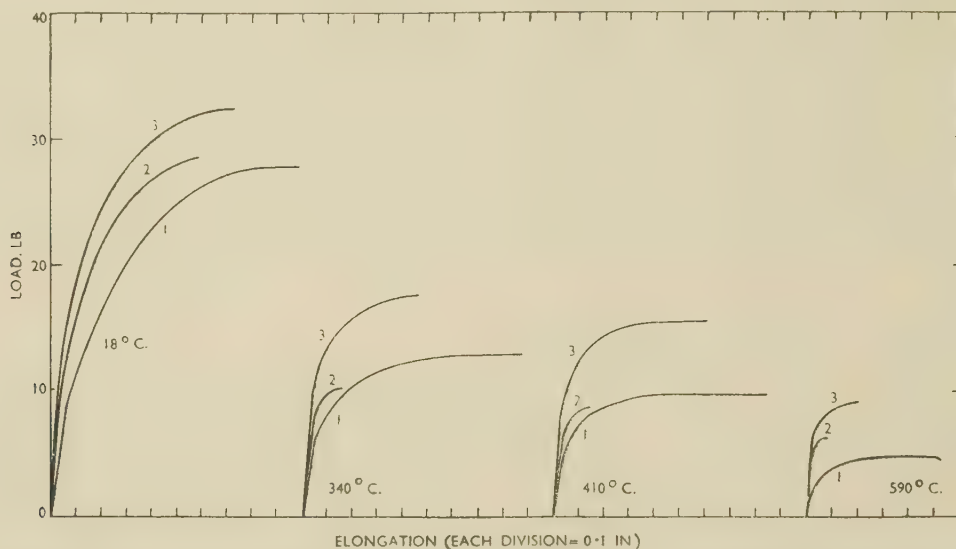


FIG. 4.—Load/Elongation Curves for Unoxidized and Oxidized Silver-0.13% Silicon Alloys Tested at 18°, 340°, 410°, and 590° C.

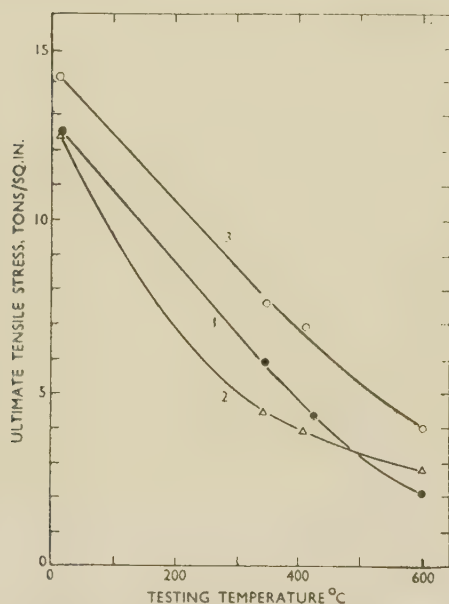


FIG. 5.—Change of Ultimate Tensile Stress with Testing Temperature for Unoxidized and Oxidized Silver-0.13% Silicon Alloys.

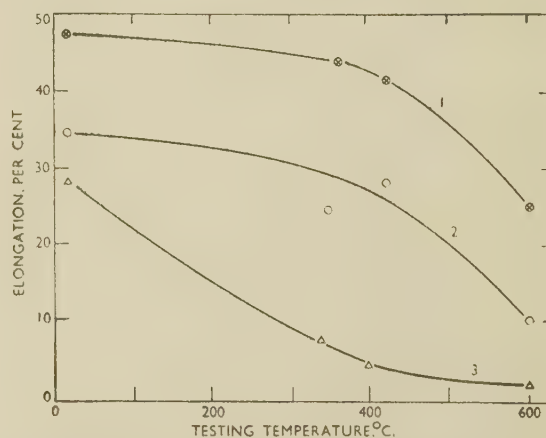


FIG. 6.—Change of Percentage Elongation with Testing Temperature for Unoxidized and Oxidized Silver-0.13% Silicon Alloys.

#### KEY TO FIGS. 4-6

- Curve 1. Vacuum-annealed at 650° C.  
 " 2. Oxidized at 650° C.; vacuum-annealed at 850° C.  
 " 3. Oxidized at 650° C.  
 All given preliminary vacuum-annealing treatment at 675° C.

the way in which the disperse phase increases the maximum load sustained and also the stress at which marked plastic deformation begins.

Figs. 5 and 6 show respectively the variations of ultimate tensile stress and elongation with testing temperature. The values of U.T.S. for the oxidized material remain above the corresponding values for the vacuum-annealed specimens at temperatures up to 590° C., clearly

tion of particles in the grain boundaries, or whether a uniform dispersion would have the same effect. A certain amount of evidence available from photomicrographs indicates that increased grain-boundary concentrations can develop during oxidation. These may be due either to increased precipitation at grain boundaries or to initial segregation of solute atoms.

In each case in Fig. 4, curve 2 illustrates the effect of



heating the oxidized specimens for 20 hr. at 850° C. in a vacuum. The effect of this treatment was to increase the concentration of particles in the grain boundaries, and interior regions developed which contained only a few particles (Fig. 16, Plate XVIII). The disperse phase appears to have only limited stability when heated in a vacuum to a temperature above that employed for oxidation, and such treatment causes a reduction in strength and an increased brittleness.

## 2. SILVER-ALUMINIUM ALLOYS

The experiments with silver-0.13% silicon alloys showed that the disperse oxide phase has a marked effect

the vacuum-annealed and in the annealed and oxidized condition only, as an additional vacuum treatment made the material too brittle to test. The curves of Fig. 7 show the marked resistance to plastic deformation, and the accompanying brittleness produced by internal oxidation. The alumina particles formed on oxidation are small compared with the silica particles, in agreement with the relative free energies of formation of the oxides. Fig. 17 (Plate XVIII) shows an electropolished specimen of alumina-containing material. This photograph is not directly comparable with those of the silver-silicon alloys, as internally oxidized silver-aluminium specimens prepared by the normal metallographic technique do not

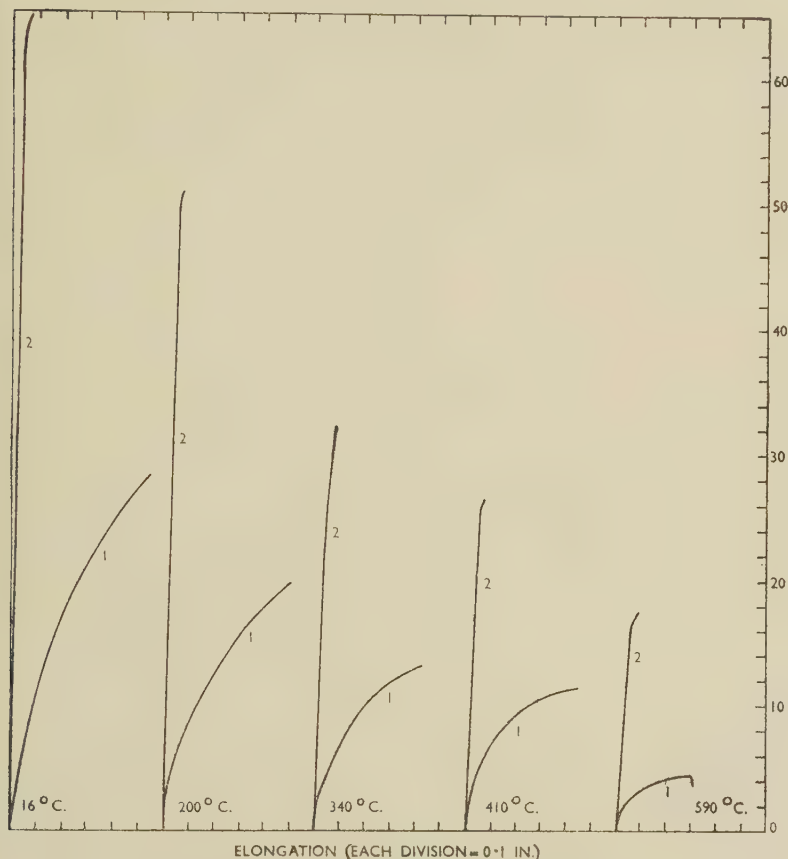


FIG. 7.—Load/Elongation Curves for Unoxidized and Oxidized Silver-0.25% Aluminium Alloys Tested at 16°, 200°, 340°, 410°, and 590° C.

KEY TO FIGS. 7 AND 8.—Curve 1. Vacuum-annealed at 675° C. Curve 2. Vacuum-annealed at 675° C.; oxidized at 650° C.

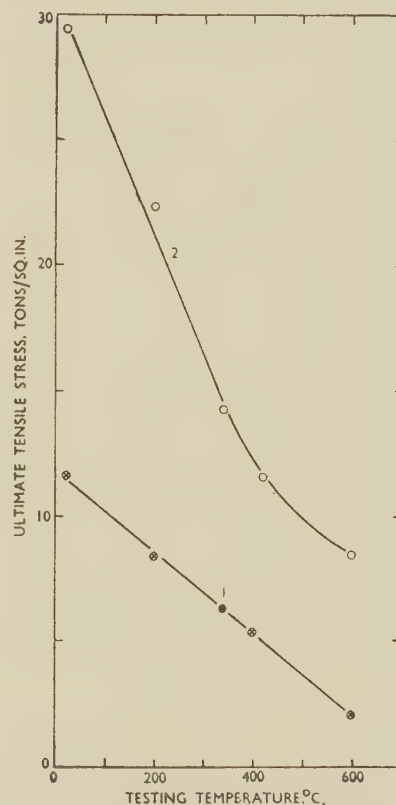


FIG. 8.—Change of Ultimate Tensile Stress with Testing Temperature for Unoxidized and Oxidized Silver-0.25% Aluminium Alloys.

in inhibiting slip. An important factor in such inhibition is the separation of the oxide particles, as this limits the distance through which dislocations can move without interference. The nature and the size of the particles are probably also of importance, although the size and separation are linked for a fixed composition of the material.

To investigate these factors further, the above experiments were repeated with a silver-0.25% aluminium alloy. This was annealed at 675° C. in a continuously evacuated alumina tube. The grain-size after this heat-treatment was somewhat larger than that obtained with silver-0.13% silicon alloy. The material was tested in

exhibit particles. It is probable that, in addition to removing the last traces of flowed material, electropolishing gives a slight electrolytic etch, thus increasing the apparent particle size. Even after this treatment, the particles are very indistinct, and little can be deduced concerning their exact size.

Fig. 8 shows the relationship between ultimate tensile stress and the temperature of testing. The ultimate tensile stress of the oxidized specimens falls off with increasing temperature, the rate of decrease being less at the high temperatures.

The results with the silver-0.25% aluminium alloy prove that a marked increase in resistance to plastic

deformation can be obtained by internal oxidation, but that at the same time there is a considerable reduction in ductility. The brittleness can be reduced, with an accompanying decrease in strength, by lowering the aluminium content of the material. Curves for silver-0.05% aluminium alloy are shown in Fig. 9. The properties of the oxidized alloy were unaltered by heating to 850° C. in oxygen, thus showing the stability of the disperse phase under oxidizing conditions. Fig. 10 shows the variation of ultimate tensile stress with testing temperature.

## VI.—ANALYSIS OF THE DISPERSE PHASE

Optical metallography of materials which have been internally oxidized does not convey much information regarding the size, shape, and nature of the disperse phase.

In order to determine these factors more fully, particles were extracted and examined by electron diffraction and

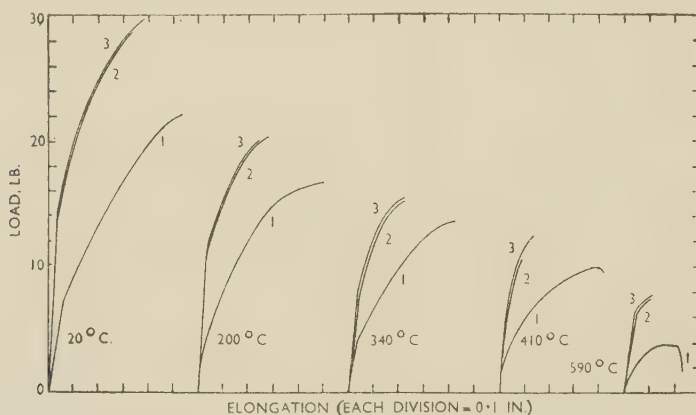


FIG. 9.—Load/Elongation Curves for Unoxidized and Oxidized Silver-0.05% Aluminium Alloys Tested at 20°, 200°, 340°, 410°, and 590° C.

### KEY

- Curve 1. Vacuum-annealed at 700° C.  
 " 2. Vacuum-annealed at 700° C.; oxidized at 650° C.; heated in oxygen at 850° C.  
 " 3. Vacuum-annealed at 700° C.; oxidized at 650° C.

electron microscopy. The extraction technique developed employed dialysis, and has subsequently been used for copper alloys.<sup>10</sup> The extracted particles from the silicon-containing material were examined by electron diffraction, and the indications were that tridymite had been formed, but the lines were too indistinct for any definite statement to be made about the structure.

Electron microscopy revealed that the particles from the silver-silicon material were clearly spherical, and the particles from the alloys containing aluminium much smaller and equiaxed.

Counts were made on the particles extracted from silver-0.13% silicon alloy oxidized at 500°, 600°, 700°, and 800° C. The estimated mean particle diameters were as follows: \*

°C.	Å.
500	250
600	330
700	440
800	740

The particles from the aluminium-containing materials were so small that size estimation was not attempted.

## VII.—DISCUSSION OF RESULTS

### 1. FACTORS AFFECTING INTERNAL OXIDATION

The effects of temperature, solute concentration, nature of the solute, and oxygen partial pressure have been described by earlier workers,<sup>4,7</sup> and the results of the present investigation are in accord with their findings.

Microhardness traverses of internally oxidized silver-0.25% aluminium alloy have shown that a considerable variation of hardness occurs from the surface to the centre of a specimen internally oxidized at a constant temperature. This is to be expected, as the rate of movement of the oxidation front is affected by both the rate of penetration of oxygen and the rate of migration of aluminium. Thus, the size and number of disperse-phase particles will change with distance from the surface and a hardness variation will result.

The present investigation has shown that internal oxidation in air can be accomplished at 650° C. through-

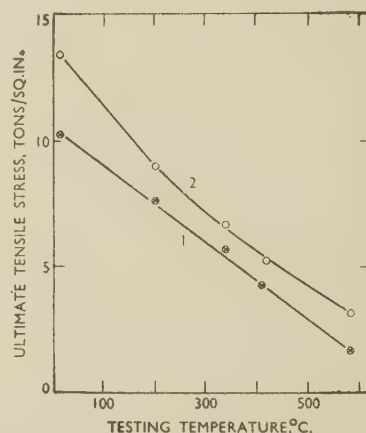


FIG. 10.—Change of Ultimate Tensile Stress with Testing Temperature for Unoxidized (Curve 1) and Oxidized (Curve 2) Silver-0.05% Aluminium Alloys.

out a section of a silver-0.13% silicon alloy with a coarse grain-size. When, however, the same conditions are applied to an alloy previously vacuum-annealed at 675° C. to give a fine grain-size, continuous oxide films result. This has been attributed to preferential diffusion of silicon along the grain boundaries in silver at 650° C. The total amount of silicon migrating outwards in a given time in a fine-grained specimen will thus be greater than that in a coarse-grained one. There is no direct evidence for this, but Hoffman and Turnbull,<sup>11</sup> in experiments on the self-diffusion of silver, have shown that for temperatures below 700° C. the apparent lattice self-diffusion coefficient in fine-grained silver is significantly larger than the true lattice diffusion coefficient found from single crystals.

### 2. TENSILE TESTS AT ROOM TEMPERATURE

The presence of a fine non-metallic dispersion has been shown markedly to increase the ultimate tensile stress at room temperature. The amount of the increase is dependent on the degree of dispersion and is particularly

\* These mean values are only approximate, since at each temperature the particle diameters varied over a wide range.



marked with the 0.25% aluminium alloy, where the ultimate tensile stress was increased to 29 tons/in.<sup>2</sup>. In this alloy, the elongation on a 2-in. gauge-length was of the order of only 1%, owing to intercrystalline brittleness.

With the equipment available, it was difficult to obtain on the wire specimens accurate values for Young's modulus, the limit of proportionality, or the proof stress, but the indications were that the increase in the last on oxidation was even more marked than the change in the ultimate tensile stress.

The recent theories proposed for the effect of hard disperse phases on the plastic properties of alloys<sup>12,13</sup> are based on the hindrance to the movement of dislocations afforded by the particles. The dependence of the strength on the degree of dispersion observed in the present investigation is to be expected from these theories.

Since the spacing of the particles in the examined materials is far smaller than the diameters of the grains, grain-size is of secondary importance when considering the hardness of internally oxidized materials. Owing, however, to the possible presence of a large number of particles in the grain boundaries, intercrystalline brittleness can be induced, and the ductility and strength can thus be affected by grain-size.

### 3. TENSILE TESTS AT ELEVATED TEMPERATURES

In order that the increase in strength imparted by the disperse phase shall be maintained at elevated temperatures, it is essential that the dispersion be stable throughout the required temperature range. Many of the precipitates formed by age-hardening are redissolved or become agglomerated on raising the temperature, but this is not generally the case with the disperse phases produced by internal oxidation. Instability has, however, been noticed when the disperse phase is heated above the oxidation temperature in a vacuum.

Tensile tests were carried out at 200°, 340°, 410°, and 590° C., and at all these temperatures the strength of the oxidized materials was greater than that of the unoxidized; there was no indication of any rapid loss in strength due to an agglomeration of the oxide. The disperse phase inhibits recrystallization and grain growth, both of which would be likely to decrease the short-time high-temperature strength.

High-temperature deformation tends to take place primarily in the grain-boundary region, but the presence of particles in these boundaries operates to prevent their sliding or migration. Dislocation movements through the grains are restricted by the particles, and the hardened grains cannot accommodate appreciable grain-boundary movements.

Although no creep or stress-rupture tests were carried out on these materials, the tests on copper alloys<sup>3</sup> containing somewhat larger oxide particles suggest that

marked decreases in creep rates are to be expected on internal oxidation.

## VIII.—CONCLUSIONS

(1) Internal oxidation has been used to produce non-metallic disperse phases in silver alloys.

(2) The effects of variables such as temperature of oxidation, nature of solute, percentage of solute, and oxygen partial pressure have been found to be in accordance with previous observations and predictions.

(3) The size of the dispersed particles varies with distance from the free surface owing to changing diffusion conditions.

(4) Grain-size can alter the diffusion rate of the solute and thus affect the particle size and type of dispersion.

(5) Grain growth and recrystallization are markedly inhibited by the fine disperse phase.

(6) The strength at room temperature is greatly increased, and the ductility decreased, by the presence of the disperse phase.

(7) The stability of the disperse phase, together with the effects noted in (5), enable the improvement in strength to be maintained at elevated temperatures.

## ACKNOWLEDGEMENTS

The authors would like to thank Professor G. W. Austin, Goldsmiths' Professor of Metallurgy in the University of Cambridge, for his encouragement and continued interest in the work. One of them (E. G.) is indebted to the Department of Scientific and Industrial Research for a maintenance allowance during the tenure of which the work was carried out.

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# A STUDY OF THE HYDROGEN-PRESSURE RELATIONSHIPS IN THE ZIRCONIUM-HYDROGEN SYSTEM\* 1726

By C. E. ELLS,† M.A., and A. D. McQUILLAN,† B.Sc., Ph.D., MEMBER

## SYNOPSIS

Measurements of hydrogen equilibrium pressure for a series of zirconium-hydrogen alloys in the composition range 1-44 at.-% hydrogen at temperatures between 500° and 950° C. have been used to deduce the form of part of the constitutional diagram for the zirconium-hydrogen system. Additions of hydrogen have been shown to cause a depression of the  $\alpha$ - $\beta$  transformation in zirconium. A eutectoid point at which the  $\beta$  solid solution is in equilibrium with the  $\alpha$  solid solution and a hydrogen-rich phase occurs at 550° C. and 32 at.-% hydrogen. The maximum solubility of hydrogen in  $\alpha$ -zirconium is 6 at.-%. It has been observed in the course of the work that small additions of hafnium (approx. 1.5 at.-%) cause a depression of the transformation temperature in zirconium, and it is concluded that the  $(\alpha + \beta)$  region in the zirconium-hafnium system must, therefore, pass through a minimum point. A reconsideration of the experimental results presented by Edwards and Levesque (*J. Amer. Chem. Soc.*, 1955, **77**, 1312) on the zirconium-oxygen-hydrogen system in the light of the present results and of Phase-Rule considerations has resulted in a proposed revision of the isothermal section of the constitutional diagram at 750° C.

## I.—INTRODUCTION

IN spite of several previous investigations, knowledge of the constitutional diagram of the zirconium-hydrogen system is still not complete, and the aim of the present work has been to establish the hydrogen-equilibrium-pressure/hydrogen-concentration/temperature relationships and phase boundaries in those regions of the system which have not already been examined satisfactorily.

The early work of Sieverts and co-workers,<sup>1,2</sup> carried out on zirconium of lower purity than that now available, established the facts that the pressure of hydrogen in equilibrium with a solution of hydrogen in metallic zirconium was sufficiently great over a wide range of temperatures and concentrations to be readily measurable, and that the processes of hydrogen evolution and absorption were reversible. After the preparation of high-purity zirconium by the iodide process, de Boer and Fast<sup>3</sup> showed that additions of hydrogen to zirconium brought about a depression of the transformation temperature and, as would be expected, an opening out of the isothermal transformation of the pure metal into a two-phase ( $\alpha + \beta$ ) region. A more complete study of the zirconium-hydrogen system was subsequently undertaken by Hall, Martin, and Rees,<sup>4</sup> but their starting material was of relatively poor quality, containing 2-3 at.-% oxygen and some hafnium as the major impurities. Recently Edwards, Levesque, and Cubicciotti<sup>5</sup> have redetermined the hydrogen-pressure/concentration/temperature relationships over the same range of temperatures and hydrogen concentrations as those examined by Hall *et al.*, using material of higher purity, while Gulbransen and Andrew<sup>6</sup> have made use of a microbalance technique to study the low-temperature region where hydrogen equilibrium pressures are below 1 mm. Hg.

The region of the zirconium-hydrogen system which has not been accurately defined by previous workers com-

prises the entire ( $\alpha + \beta$ ) phase field and the eutectoid horizontal. With the present results, however, the zirconium-hydrogen system is now as well understood as the very similar titanium-hydrogen system, previously studied by one of us.<sup>7</sup> Although our experimentally determined relationships are sufficiently accurate for such a purpose, a full thermodynamic analysis of the results, such as was undertaken by Gulbransen and Andrew, has not been carried out because the purity of our zirconium, and indeed of that used in all previous investigations, is not, in our opinion, sufficiently high for the results to be of any great significance.

## II.—EXPERIMENTAL METHODS

### 1. MATERIAL USED

Two types of zirconium were available for this work, one containing very little oxygen but about 1.5 at.-% hafnium and the other substantially hafnium-free but containing about 0.09 at.-% oxygen. Except for a single comparison experiment, the hafnium-free zirconium was used throughout the work, as it was felt that the presence of as much as 1.5 at.-% hafnium in the starting material would have a very pronounced effect on the phase relationships deduced from measurements of hydrogen equilibrium pressures. It is apparent from our results that the amount of impurity in the hafnium-free zirconium was, however, sufficient to cause some slight departure from the behaviour to be expected of a true binary zirconium-hydrogen solid solution. The impurity content of the hafnium-free zirconium was: oxygen 0.085, silicon 0.05, iron 0.02, titanium 0.01, copper 0.006, hafnium 0.01 at.-%.

### 2. APPARATUS

It was expected, from the results of previous workers, that pressures in the region of the zirconium-hydrogen

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system selected for study would lie in the range 30–0.3 mm. Hg. This pressure range can be conveniently measured with a dibutyl phthalate manometer (*d* 1.045 g./c.c.). In order, however, to link our results with those of Gulbransen and Andrew<sup>6</sup> at low pressures, a Pirani gauge capable of measuring pressures down to  $10^{-3}$  mm. Hg. was incorporated in the apparatus. The accuracy of the Pirani gauge readings was, of course, lower than that obtained by using the manometer which, when observed with a cathetometer, was capable of measuring to within  $\pm 0.02$  mm.

The apparatus used in this work is basically very similar to that described by McQuillan,<sup>7</sup> and is shown diagrammatically in Fig. 1. The zirconium specimen is contained in a clear silica tube. Hydrogen, generated

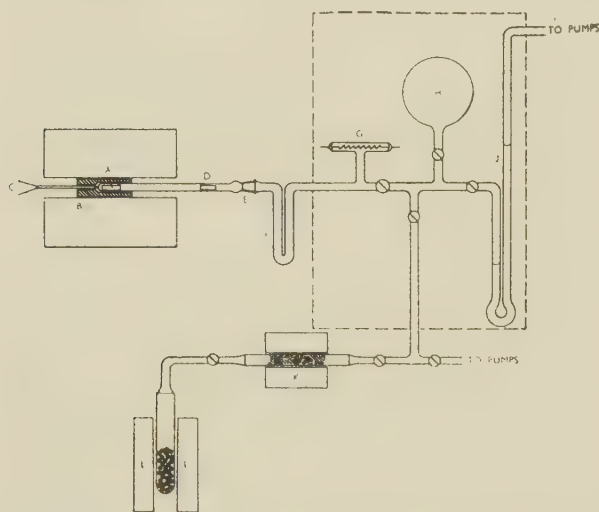


Fig. 1.—Diagrammatic Representation of the Apparatus Used for Establishing Hydrogen-Equilibrium-Pressure Relationships.

#### KEY

- |   |                               |
|---|-------------------------------|
| A Specimen.                                     | F Liquid-air trap.            |
| B Nickel-chromium temperature-equalizing block. | G Pirani gauge.               |
| C Thermocouple.                                 | H Hydrogen reservoir.         |
| D Magnetically operated nickel pusher.          | J Manometer.                  |
| E Silica-to-glass cone joint.                   | K Hydrogen-purification tube. |
|   | L Hydrogen generator.         |

The constant-temperature enclosure is denoted by a broken line.

by heating pellets of titanium hydride and further purified by passing over titanium turnings at about  $900^{\circ}\text{C.}$ , is collected in a bulb of accurately known volume at a measured temperature and pressure, and is subsequently admitted to the evacuated and outgassed specimen tube and allowed to dissolve in the heated zirconium specimen. During an experimental run, the specimen tube and the operative pressure-measuring device are isolated from the remainder of the system by means of vacuum taps. The whole apparatus is capable of being evacuated initially to a pressure of  $10^{-6}$  mm. Hg.

### 3. ACCURACY AND ERRORS

In order to obtain a high degree of accuracy in the results, the experimental procedure outlined in the previous section was refined in a number of ways which both ensured that the measurements themselves were as accurate as possible and reduced the contamination suffered by the specimen during the work to a negligible amount.

The major potential source of error in an apparatus of this type lies in the determination of the concentration of hydrogen in the specimen. If, for instance, full use is to be made of the accuracy with which the volume of the hydrogen reservoir and the pressure of the gas within it can be measured, the temperature of the bulb must be kept constant to within  $0.1^{\circ}\text{C.}$  at least. Under these conditions the amount of hydrogen actually admitted to the system can be calculated to better than one part in a thousand. All the gas admitted to the system, however, is not dissolved in the heated specimen, and in calculating the concentration of hydrogen dissolved in the metal, allowance must be made for the small quantity of gas remaining outside the specimen to set up the equilibrium hydrogen pressure within the system. This is a function of the internal volume of the closed part of the apparatus, and it is advisable, therefore, to keep the necessary correction as small as possible by reducing the internal volume of the system to a minimum. The correction, furthermore, will also be affected by the temperature of the gas which remains outside the metal, and it can be computed with greater accuracy if the whole of the closed part of the apparatus, other than a short length of silica tube in which the specimen is contained, is maintained at a constant temperature. In the experiments described, therefore, the greater part of the apparatus, including the hydrogen reservoir bulb, was surrounded by a constant-temperature enclosure. The additional allowance to be made for the fraction of the gaseous hydrogen in the heated part of the specimen tube was calculated from the results of an experiment in which observations were made of the change of hydrogen pressure with the temperature of the silica tube when no specimen was present. The amount of hydrogen admitted to the system during this blank run was adjusted to give pressures comparable with the equilibrium pressures set up in the presence of a zirconium specimen. Errors due to temperature fluctuations were reduced to a level which permitted full advantage to be taken of the accuracy with which the pressure and hydrogen-concentration measurements could be made by controlling the specimen temperature to within  $\pm 0.1^{\circ}\text{C.}$

The most difficult part of the present series of experiments was the prevention of contamination of the zirconium specimen during the course of the work. Since zirconium is a highly reactive metal with a great affinity for oxygen, nitrogen, and carbon, it will, when heated, absorb any gases containing these elements that may enter the system. It has been demonstrated<sup>8</sup> that a considerable amount of water vapour may be evolved from heated glass, and it would appear from our experiences that this is also the case for heated silica. Contamination from this source was eliminated by a preliminary out-gassing process which involved heating as much as possible of the apparatus under vacuum. The part of the silica specimen tube which would be heated during an actual experimental run was maintained at  $950^{\circ}\text{C.}$  for at least 24 hr. Since it is impossible to open the system to air after degassing without absorbing further gas on the glass and silica walls, the specimen had to be put in the specimen tube before the out-gassing process began, but in order to prevent it from absorbing the liberated gases, it was first placed in the unheated part of the specimen tube and subsequently moved to its working position by means of a magnetically



operated pusher. The risk of contamination was further reduced by incorporating a liquid-air trap in the system. These precautions limited the pressure rise within the sealed system to about  $10^{-3}$  mm. Hg/hr. in a volume of 25 c.c. when the empty specimen tube was heated to  $950^{\circ}\text{C}$ . If it is assumed that this gas is oxygen and that it is all absorbed by the heated specimen, then the rate of contamination of the specimen would amount to  $5 \times 10^{-5}$  at.-%/hr., but since the heated specimen and the liquid-air trap are in competition for the condensable vapour evolved in the system, the maximum rate of specimen contamination is probably rather greater than this. The maximum rate, however, applies only when the specimen tube is heated to  $950^{\circ}\text{C}$ , and as the specimen spends a relatively small part of the total time required for a series of experiments at this temperature, and the

hydrogen concentrations, repetition of an experiment at any particular concentration after several intervening runs gave a curve identical with that of the original experiment to within the limits of the expected error in the measurements. Furthermore, the hydrogen-pressure/temperature curves obtained at any one hydrogen concentration were truly reversible, no hysteresis effects being observed on heating and cooling.

#### 4. PLOTTING OF RESULTS

Owing to the finite volume of the system, the pressure/temperature curves obtained by direct experiment do not correspond to constant hydrogen concentration within the specimen. The actual hydrogen concentration corresponding to any pressure and temperature reading can, however, be calculated, and the results

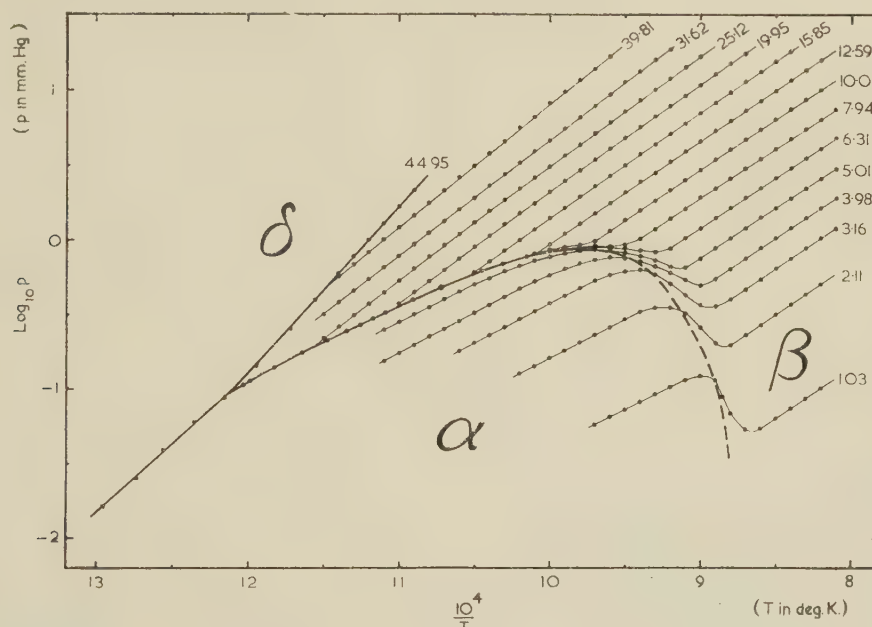


FIG. 2.—Hydrogen-Pressure/Concentration/Temperature Relationships in the Zirconium-Hydrogen System Obtained from the Present Work. The curves representing two-phase regions have been drawn in heavier lines. The higher-temperature part of the curve denoting the  $(\alpha + \beta)$  region is shown as a broken line which indicates its most probable position in an oxygen-free system. The numbers on the curves denote the hydrogen concentration in atomic per cent.

rate of gas evolution from the silica tube, furthermore, decreases exponentially with the temperature, the mean rate of contamination throughout the whole course of the experiment is undoubtedly below  $10^{-5}$  at.-% oxygen/hr. The amount of impurity introduced into our specimen of zirconium during an experiment is, therefore, negligibly small compared with that initially present. Impurity pick-up by direct reaction between the specimen and the material of the specimen tube was prevented by lining the heated end of the silica tube with thin molybdenum sheet. The only remaining source of contamination, i.e. impurities present in the hydrogen admitted to the system, was eliminated by the preliminary purification of the hydrogen.

The success of the precautions taken was indicated by the fact that throughout the whole course of this work no effects which could be attributed to contamination of the specimen during the experiments were observed. Although the same specimen was used a number of times for experiments carried out at a series of different

plotted as a series of pressure/concentration isothermals, from which true pressure/temperature curves at constant composition can be drawn.

### III.—EXPERIMENTAL RESULTS

The hydrogen-equilibrium-pressure/temperature relationships for a range of hydrogen concentrations are presented in Fig. 2, in which pressure  $p$  is plotted on a logarithmic scale and temperature is expressed in terms of the reciprocal of the absolute temperature  $T$ . In a single-phase region, the quantity  $R \left( \frac{\partial \ln p}{\partial \frac{1}{T}} \right)_c$ , where  $R$  is

the gas constant, represents the heat of solution of one gramme-molecule of hydrogen in the metal. Since this quantity is almost independent of temperature, the  $\log p/\frac{1}{T}$  curves are approximately linear and the  $\alpha$  and  $\beta$

phase fields can be easily recognized. In a true binary system, the equilibrium pressure within a two-phase region is a function of temperature, but not of concentration, and such a region is, therefore, represented on the diagram by a single curve for all alloy compositions. If, however, the specimens are impure and the system no longer a true binary, this condition will not be rigorously applicable, although when the amount of impurity is

line at temperatures above 750° C. In drawing the broken line corresponding to the high-temperature part of the  $(\alpha + \beta)$  region through the points representing the beginning of  $\beta$ -phase formation in  $\alpha$ -phase material, rather than through those representing the converse process, it was borne in mind that oxygen additions to zirconium elevate the  $\alpha$ - $\beta$  transformation temperature. In their work on the constitutional diagram of the

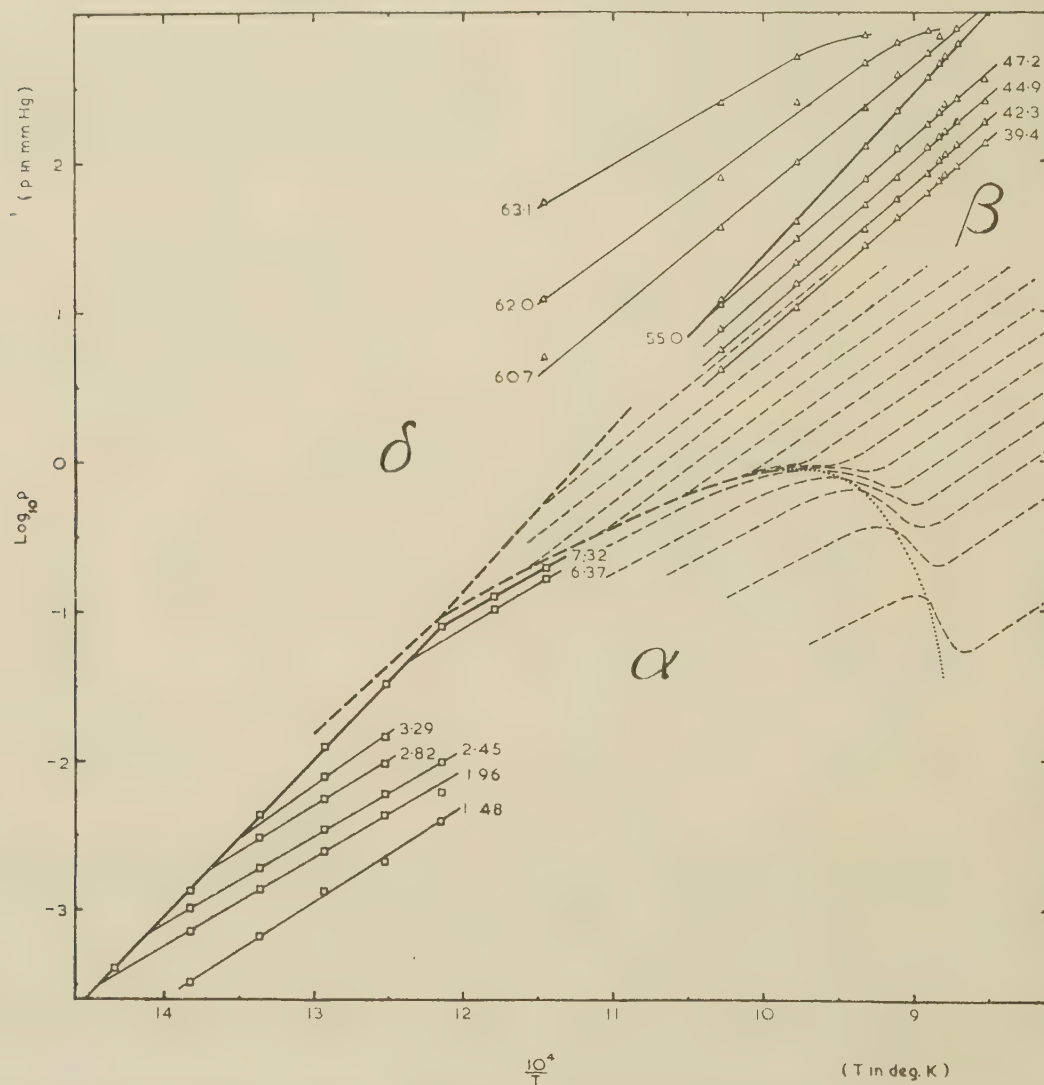


FIG. 3.—Hydrogen-Pressure/Concentration/Temperature Relationships for the Zirconium-Hydrogen System as Obtained by Edwards, Levesque, and Cubicciotti,<sup>5</sup> Gulbransen and Andrew,<sup>6</sup> and the Present Authors.

—△— Edwards, Levesque, and Cubicciotti.<sup>5</sup> —□— Gulbransen and Andrew.<sup>6</sup> --- Present authors.

The numbers on the curves denote the hydrogen concentration in atomic per cent.

small, the departure from ideal behaviour will not be marked.

In Fig. 2, three two-phase regions can be ascertained. These are represented by a markedly non-linear  $(\alpha + \beta)$  curve and two straight lines denoting the  $(\beta + \delta)$  and  $(\alpha + \delta)$  fields. The effect of the small amount of oxygen present in the zirconium is most noticeable in connection with the  $(\alpha + \beta)$  curve, which, on the basis of the present experimental results, should in fact be represented by a fairly broad band rather than by a single

zirconium-oxygen system, Domagala and McPherson<sup>9</sup> have shown that, although oxygen additions produce a marked increase in the temperature of the  $\beta/(\alpha + \beta)$  boundary, the effect on the  $\alpha/(\alpha + \beta)$  boundary is quite small. The presence of some oxygen in our alloys, therefore, will have little effect on the temperature at which the  $\alpha$  phase begins to transform, and it is considered that the broken line in Fig. 2 will be only slightly above the true  $(\alpha + \beta)$  curve for the ideally pure zirconium-hydrogen system.



The results presented in Fig. 2 enable us to plot the boundaries of the  $(\alpha + \beta)$  and part of the  $(\beta + \delta)$  and  $(\alpha + \delta)$  fields on the constitutional diagram. These results, together with data derived from the work of Edwards, Levesque, and Cubicciotti<sup>5</sup> and of Gulbransen and Andrew,<sup>6</sup> which are presented in Fig. 3, give a fairly complete picture of the constitutional diagram of the system up to a hydrogen concentration of 60 at.-%, as shown in Fig. 4. It can be seen that hydrogen produces a marked depression of the transformation in zirconium. This is contrary to the findings of Edwards, Levesque, and Cubicciotti,<sup>5</sup> who suggest that

higher than in the titanium-hydrogen system,<sup>7,11</sup> where the eutectoid reaction occurs at about 300° C. Lenning, Craighead, and Jaffee<sup>11</sup> have shown that the eutectoid reaction in the titanium-hydrogen system exhibits a considerable hysteresis effect on heating and cooling, and the exact position of the eutectoid horizontal in this system is, therefore, still in doubt. In order to see whether a similar effect occurs in the eutectoid reaction in the zirconium-hydrogen system, an alloy containing 13.41 at.-% hydrogen was selected for more detailed study. The results of this work have been plotted on an enlarged scale in Fig. 5 in order to compare more readily

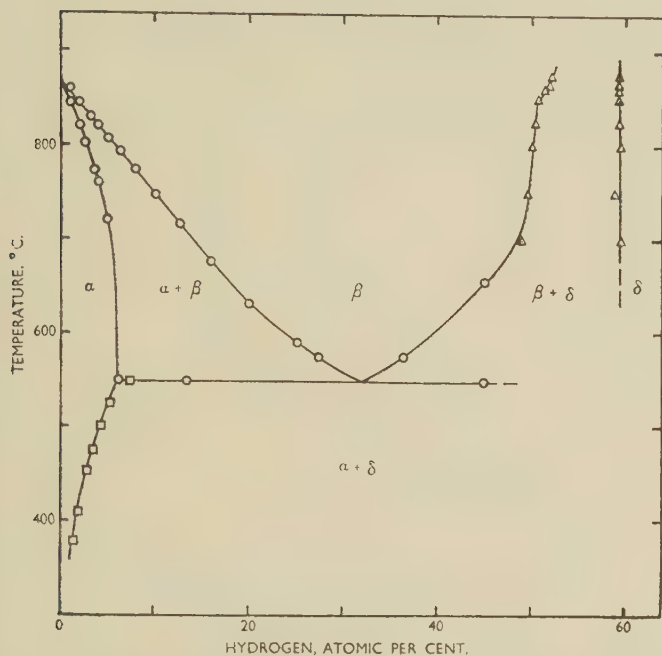


Fig. 4.—Constitutional Diagram of the Zirconium-Hydrogen System in the Composition Range 0–60 at.-% Hydrogen, Derived from the Relationships Shown in Fig. 3.

- △ Edwards, Levesque, and Cubicciotti.<sup>5</sup>
- Gulbransen and Andrew.<sup>6</sup>
- Present authors.

hydrogen causes very little depression in the transformation temperature of zirconium and no appreciable opening out of the transformation into a  $(\alpha + \beta)$  field, in spite of the fact that the known large latent heat of transformation of zirconium<sup>10</sup> requires the existence of a wide  $(\alpha + \beta)$  region on thermodynamic grounds. Comparison of our results with those of Edwards *et al.*<sup>5</sup> given in Fig. 3, shows that the temperature and concentration region studied by these workers did not, in fact, cover the  $\alpha$  or  $(\alpha + \beta)$  phase regions, as they appeared to believe, but that their work was confined entirely to the  $\beta$  phase and phases of higher hydrogen content.

In Fig. 2, it can be seen that the pressure/temperature curves representing the  $(\alpha + \beta)$ ,  $(\beta + \delta)$ , and  $(\alpha + \delta)$  regions in the constitutional diagram intersect at a triple point which defines the  $\beta \rightleftharpoons \alpha + \delta$  eutectoid horizontal. The eutectoid temperature in the zirconium-hydrogen system is  $547^\circ \pm 2^\circ \text{C.}$  and is, therefore, appreciably

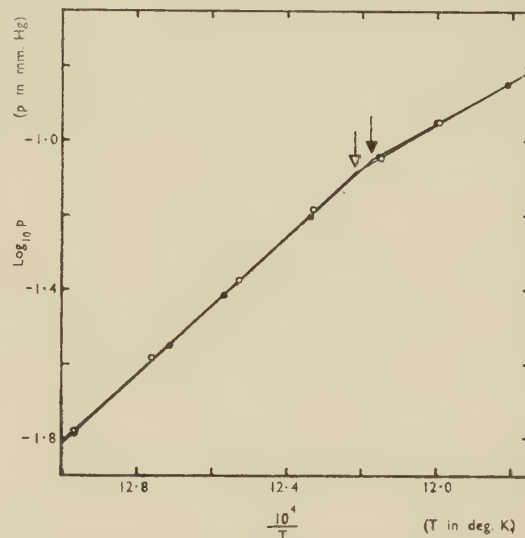


Fig. 5.—Hydrogen-Pressure/Temperature Curve for a Zirconium-Hydrogen Alloy Containing 13.41 at.-% Hydrogen as Obtained on Heating and Cooling.

- Results obtained in heating experiments.
- Results obtained in cooling experiments.

The arrows indicate the positions of the discontinuities in slopes in the two curves.

the pressure/temperature curves obtained by heating and by cooling experiments. The sharp discontinuities in the slope of the  $\log p / \frac{1}{T}$  curves representing the reaction  $(\alpha + \beta) \rightleftharpoons (\alpha + \delta)$  are easily recognized, and it can be seen that the degree of thermal hysteresis is small, amounting to slightly less than 4° C. In these experiments, the specimen was maintained at each temperature represented by a point on the diagram until no further change in hydrogen pressure was detectable. A period of about 1 hr. appeared to be necessary.

The pressure/concentration/temperature relationships determined by Gulbransen and Andrew<sup>6</sup> for the zirconium-hydrogen system lie in a region of lower pressure and temperature than our results, except for the high-temperature part of the curve for their 7.32 at.-% hydrogen alloy. Only in this one instance, therefore, can the two sets of results be compared directly. Such comparison as can be made reveals no serious difference

in the actual experimental results, but there is, however, an apparent difference in interpretation. The  $\log p/\frac{1}{T}$  curve for the 7.32 at.-% hydrogen alloy consists of two intersecting straight lines. Gulbransen and Andrew consider that the lower-temperature line represents the two-phase ( $\alpha + \delta$ ) region and that the higher-temperature line is one of the group of lines of constant hydrogen concentration which together represent the single-phase  $\alpha$  field. According to our results, however, the 7.32 at.-% alloy passes directly from the ( $\alpha + \delta$ ) region to the ( $\alpha + \beta$ ) region at the temperature of the eutectoid, and never attains the single-phase  $\alpha$  state. The higher-temperature line on our interpretation, therefore, represents the two-phase ( $\alpha + \beta$ ) region, and not one of the lines in the  $\alpha$ -phase region. We have observed that the

fairly complete picture of both the constitutional diagram and the pressure/concentration/temperature relationships in the zirconium-hydrogen system up to hydrogen concentrations of about 60 at.-%, there remain some small points of disagreement between the results of the various workers in addition to the major differences of interpretation already mentioned. It would seem probable that the greater part of the disagreement can be attributed to the presence of different amounts and types of impurities in the samples of zirconium used by the various workers. The principal difference between our sample and those of the other two groups of workers is that ours was free of hafnium, but contained a little oxygen; whereas those of the previous workers<sup>5,6</sup> contained appreciable quantities of hafnium and probably rather less oxygen. Hall, Martin, and Rees<sup>4</sup>

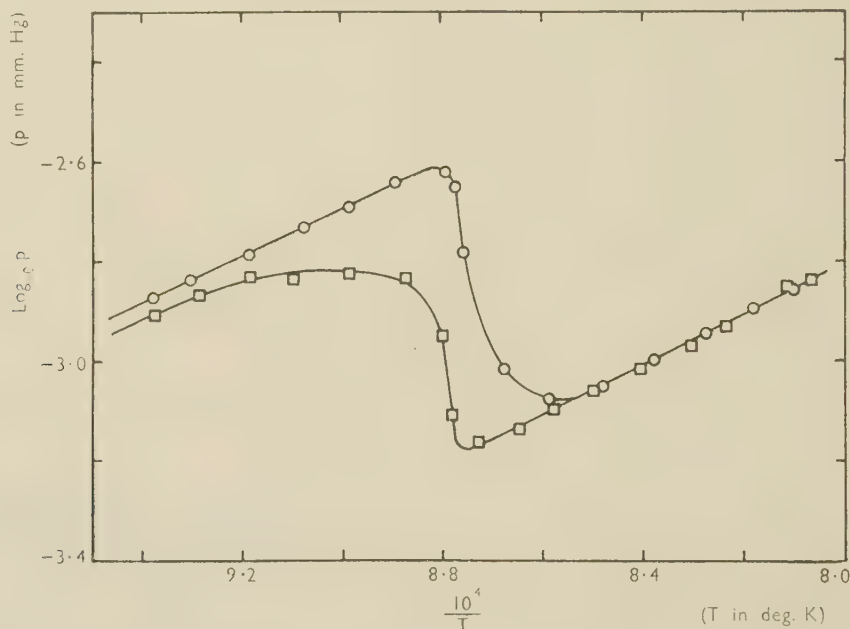


FIG. 6.—Hydrogen-Pressure/Temperature Curves for Two Samples of Iodide-Refined Zirconium at a Hydrogen Concentration of 0.13 at.-%.

- Sample containing 1.5 at.-% hafnium and having low oxygen content.
- Hafnium-free sample containing a higher concentration of oxygen.

lines of constant hydrogen concentration in the  $\alpha$ -phase region do lie almost parallel to the line representing the ( $\alpha + \beta$ ) region, and on this account some confusion between the two types of curve is not surprising. It will be seen in Fig. 3, however, that the increase in pressure level of Gulbransen and Andrew's curve for the 7.32 at.-% hydrogen alloy is appreciably smaller than would be expected from the trend shown by the rest of the family of curves, which suggests that the curve in question is of a different nature from the rest and provides strong support for our contention that it is, in fact, the ( $\alpha + \beta$ ) curve. Furthermore, interpreted in this way, Gulbransen and Andrew's results are consistent with the position of our  $\alpha/(\alpha + \beta)$  boundary, which would not otherwise be the case.

#### IV.—DISCUSSION OF RESULTS

Although the present results, when taken in conjunction with previously published information, give a

have shown that the presence of oxygen in zirconium-hydrogen alloys increases the equilibrium hydrogen pressure, and it is not surprising, therefore, that our pressure/temperature curves in both the  $\alpha$ - and  $\beta$ -phase fields appear to be slightly above those presented in the earlier publications. A further difference lies in the fact

that the slope  $\left(\frac{\partial \ln p}{\partial \frac{1}{T}}\right)_c$  of our curves is smaller than that

observed by the other workers for the  $\alpha$ - and  $\beta$ -phase regions. The most obvious explanation for this appears to be that the presence of hafnium in the zirconium increases the heat of solution of hydrogen in the material, but this view is unfortunately contradicted by direct comparative experiments on our sample of oxygen-bearing hafnium-free zirconium and on a sample of zirconium containing about 1.5 at.-% hafnium and very little oxygen. The  $\log p/\frac{1}{T}$  curves for the two types of



zirconium containing 0.13 at.-% hydrogen are presented in Fig. 6, and it can be seen that the slopes  $\left(\frac{\partial \ln p}{\partial \frac{1}{T}}\right)_c$  in

both the  $\alpha$ - and  $\beta$ -phase regions are the same for the two samples. Unless the slight discrepancies in slope of the  $\log p/\frac{1}{T}$  curves of the various workers can be accounted

for by the presence of other impurities, it must be assumed that, since the only obvious remaining difference between the three sets of results is the temperature range in which they were determined, the heats of solution of hydrogen in  $\alpha$ - and  $\beta$ -zirconium cannot be considered to be independent of temperature when the temperature varies over a wide range.

The curves shown in Fig. 6 can also throw some light on the nature of the zirconium-hafnium and zirconium-oxygen systems. The amount of hydrogen added to the

depresses the  $\alpha$ - $\beta$  transformation in zirconium. Fast<sup>12</sup> has shown that large additions of hafnium to zirconium elevate the transformation temperature, and it has sometimes been assumed that small amounts of hafnium do likewise. From the present results, however, it is apparent that the  $(\alpha + \beta)$  region in the zirconium-hafnium system very probably goes through a minimum point. For the oxygen-bearing sample of zirconium, the transformation range is 865°–905° C., thus showing that oxygen elevates the transformation temperature in agreement with the findings of Domagala and McPherson.<sup>9</sup>

The results obtained in the present work on the position of the  $(\alpha + \beta)$  region in the zirconium-hydrogen system have some bearing on the form of the constitutional diagram for the ternary zirconium-oxygen-hydrogen system proposed by Edwards and Levesque,<sup>13</sup> since these authors have, as previously pointed out, mistaken the nature of the binary zirconium-hydrogen

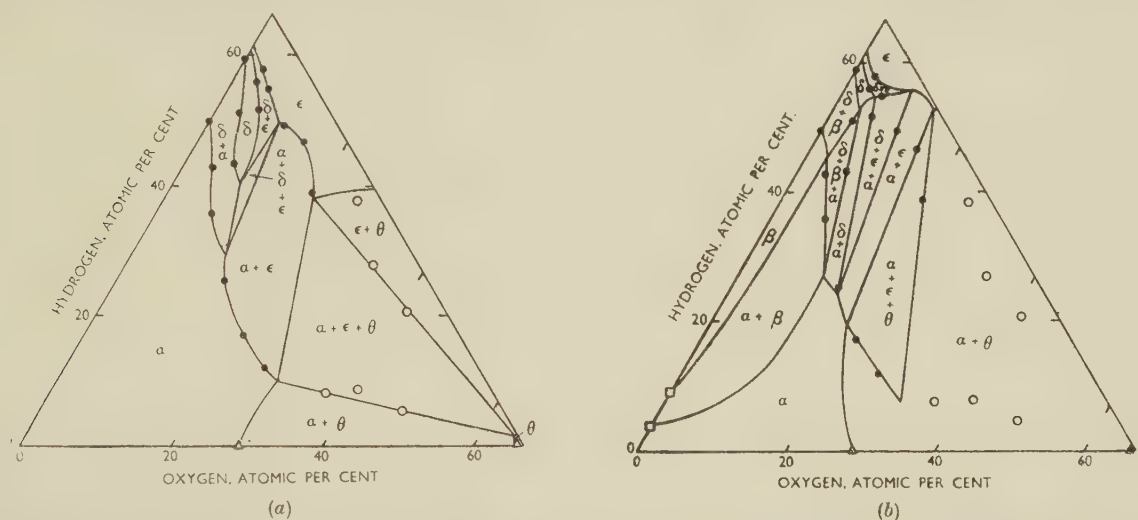


Fig. 7.—Isothermal Section of the Constitutional Diagram of the Zirconium-Oxygen-Hydrogen System at 750° C. after Edwards and Levesque<sup>13</sup> (a) and the present authors' reinterpretation of the same section (b). The  $\theta$  phase is the compound  $\text{ZrO}_2$ .

● Edwards and Levesque,<sup>13</sup> ○ Hall, Martin and Rees,<sup>4</sup> ▲ Domagala and McPherson,<sup>9</sup> □ Present work.

Insufficient data are at present available to allow the oxygen-rich corner of the modified diagram to be drawn.

hafnium-bearing and oxygen-bearing samples of zirconium to give the curves in question was very small (0.13 at.-%) and would, by itself, have an almost negligible effect on the temperature of the  $\alpha$ - $\beta$  transformation in pure zirconium. The hafnium and oxygen impurities, however, though they have very little effect on the pressure/temperature relationships for the  $\alpha$ - and  $\beta$ -phases, would be expected to bring about a spreading of the  $\alpha$ - $\beta$  transformation, and to result in the formation of an  $(\alpha + \beta)$  region. Such an effect can be seen in both the curves illustrated in Fig. 6, in which the isothermal discontinuity in the pressure/temperature curves which occurs when the metal is pure is replaced by a non-linear curve, representing the region in which the  $\alpha$  and  $\beta$  phases can co-exist, spreading over an appreciable temperature range. The point of interest is the precise range of temperature covered by the  $(\alpha + \beta)$  region in the two materials. In the case of the hafnium-bearing sample of zirconium, it extends from 865° to 800° C., and it is apparent, therefore, that hafnium

system and in particular the extent of the  $\alpha$ -phase region. In attempting a reinterpretation of their results on the ternary system, it was realized that they had made another and more far-reaching error of interpretation, since in drawing the phase boundaries in their isothermal sections of the constitutional diagram, they have assumed that regions of invariant pressure in the isothermal hydrogen-pressure/hydrogen-concentration curves for zirconium-oxygen-hydrogen alloys represent two-phase regions. The Phase Rule indicates, however, that in a ternary system, only three-phase regions will exhibit an invariant vapour pressure of any one component. Some idea of the true nature of the zirconium-oxygen-hydrogen system can, however, be obtained by redrawing the isothermal sections presented by Edwards and Levesque in accordance with our present knowledge of the binary system and the requirements of the Phase Rule, using the pressure/concentration curves given by these authors. The available data proved to be insufficient for detailed work, and a reinterpretation of

only a single isothermal section at 750° C. was carried out. The modified isothermal section, together with the corresponding original diagram of Edwards and Levesque, is shown in Fig. 7. In putting forward the new isothermal section of the zirconium-oxygen-hydrogen diagram, the present authors suggest only that it is a more reasonable interpretation of existing results; much more work would be required to establish the diagram exactly.

## ACKNOWLEDGEMENTS

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# THE CONSTITUTION OF COPPER-RICH ALLOYS OF THE COPPER-MANGANESE-ALUMINIUM SYSTEM \*

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## SYNOPSIS

The constitution of copper-based alloys containing approximately 0–30 wt.-% manganese and 0–18 wt.-% aluminium has been determined within the temperature range 800°–400° C., and the results are presented in the form of isothermal sections. The  $\beta$  phase is stable over a wide range of compositions at high temperatures (e.g. 800° C.), but its stable range decreases as the temperature falls,  $\beta$ -manganese,  $\alpha$ , and  $\gamma$  being precipitated. A ternary phase,  $\text{Cu}_3\text{Mn}_2\text{Al}$ , forms by the peritectoid reaction  $\beta + \beta\text{-Mn} \rightleftharpoons \text{Cu}_3\text{Mn}_2\text{Al}$  at temperatures below approximately 550° C. This phase has a face-centred cubic structure with  $a = 6.89 \text{ kX}$ , the unit cell containing 24 atoms. Two ternary peritectoid reactions occur: (1)  $(\beta + \beta\text{-Mn}) \rightleftharpoons (\alpha + \text{Cu}_3\text{Mn}_2\text{Al})$ . The composition of the peritectoid point is approximately 17 wt.-% manganese and 8 wt.-% aluminium, and the temperature lies between 550° and 525° C. (2)  $(\beta + \beta\text{-Mn}) \rightleftharpoons (\gamma + \text{Cu}_3\text{Mn}_2\text{Al})$ . The composition of this peritectoid point is approximately 13 wt.-% manganese and 12 wt.-% aluminium, and the temperature is between 450° and 425° C. At a temperature within the approximate limits 420°–400° C.,  $\beta$  phase of composition approximately 6 wt.-% manganese and 12 wt.-% aluminium decomposes eutectoidally in the reaction  $\beta \rightleftharpoons (\alpha + \gamma + \text{Cu}_3\text{Mn}_2\text{Al})$ . High-temperature X-ray experiments have confirmed that the  $\beta$  phase has a disordered body-centred cubic structure at high temperatures, and this changes to ordered  $\beta_1$  on cooling. Ordering takes place over a range of composition; for alloys whose compositions lie on a line between  $\text{Cu}_3\text{Al}$  and  $\text{Cu}_2\text{MnAl}$  it occurs at temperatures ranging approximately from 550° to 625° C.

## I.—INTRODUCTION

COMMERCIAL aluminium bronzes often contain manganese, and recently an aluminium bronze alloy containing about 12% manganese, together with several per cent. of iron and nickel, has found important commercial applications.<sup>1</sup> Although during the past fifty years the copper-rich alloys of the copper-manganese-aluminium system have been the subject of a number of investigations, the information on their constitution is limited. In 1903, Heusler<sup>2</sup> reported the ferromagnetic properties of some of the alloys, and the term "Heusler alloys" has been adopted to describe these and ferromagnetic alloys of certain other systems. Rosenhain and Lantsberry<sup>3</sup> investigated the mechanical properties of alloys containing up to approximately 10%  $\frac{1}{2}$  of both manganese and aluminium, while Dean *et al.*<sup>4</sup> determined the mechanical properties of the wrought  $\alpha$  solid solutions containing up to 50% manganese.

The binary copper-aluminium system has been reviewed by Raynor.<sup>5</sup> The most recent determination of the copper-manganese phase diagram is that of Dean *et al.*<sup>6</sup> The manganese-rich portion of the manganese-aluminium system has been determined by Köster and Bechtold.<sup>7</sup> Although the Heusler alloys have been studied to determine the relationship between ferromagnetic and other physical properties, on the one hand, and crystallographic structure and alloy constitution, on the other, no comprehensive determination of

the phase relationships has been reported. The liquidus surface of the copper-rich portion of the ternary system has been studied by Krings and Ostmann.<sup>8</sup> Dean *et al.*<sup>9</sup> established the limits of the  $\alpha$  solid-solution field at temperatures ranging from 850° to 400° C., but although some information is also given concerning the adjacent phase regions, these were not fully established. Haworth and Hume-Rothery<sup>10</sup> have determined the effect of manganese on the  $\alpha/(\alpha + \beta)$  and  $(\alpha + \beta)/\beta$  phase boundaries at 672° C.

The present paper reports the results of experiments to determine the influence of manganese on the range of stability and the decomposition of the  $\beta$  phase. Isothermal sections have been constructed representing the constitution of alloys within the compositional range of approximately 0–30% manganese and 0–18%  $\frac{1}{2}$  aluminium at temperatures from 800° to 400° C.

## II.—MATERIALS AND EXPERIMENTAL METHODS

The materials used in the preparation of the alloys were electrolytic copper and manganese and super-purity aluminium. Copper-manganese hardener alloys containing about 33% manganese were first prepared. Ingots of the ternary alloys weighing about 150 g. were then made by melting, in a gas-fired furnace, copper and the hardener, and finally adding aluminium. Alumina-lined crucibles were used. Each alloy was cast into a

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‡ All values given in the paper are in wt.-%.

chill mould, then rapidly re-melted and re-cast in order to ensure adequate mixing and to avoid gas unsoundness. Alloys containing up to approximately 12% aluminium were hot forged, and all the alloys were annealed for 6 days at 750° C. and quenched.

For the construction of the isothermal sections, specimens were cut from the quenched bars, annealed until it was estimated that equilibrium had been established, and water-quenched. The specimens were then sectioned, polished, and examined microscopically, usually after etching electrolytically in 1% chromic acid solution. Annealing of microspecimens was carried out in air, the temperature control being usually within  $\pm 3^\circ$  C.

Frequent use was made of quantitative metallography by the "point-count" method,<sup>11</sup> as an aid to determining the location of phase boundaries, while micro-hardness determinations were of considerable assistance in distinguishing between constituents of somewhat similar etching characteristics. X-ray-diffraction examination was carried out at room temperature on powder samples from selected alloys. Filings were taken from microspecimens which had been annealed to equilibrium; the filings were sealed *in vacuo* and re-annealed at the same temperature as the microspecimens for 1 hr. and then quenched. X-ray examination was also made of several alloys at elevated temperatures.

About half the total number of alloys were analysed chemically, the samples for analysis having been quenched from 800° C. The copper, manganese, and aluminium contents were directly determined, and, in representative samples, the iron and silicon contents also. In the isothermal sections (Figs. 1-8) analysed alloys are marked with a vertical bar. The analytical totals lay within the limits 99.9 and 100.1%. The iron content of the alloys was of the order of 0.01%. A series of alloys made from one copper-manganese hardener contained up to 0.07% silicon, whereas alloys made from the second hardener contained less than 0.005% silicon. The microstructures of the former series showed small grey particles, which were unidentified, but the positions of the phase boundaries in the isothermal sections were in agreement in both series.

Generally, the specimens were brought to the temperature of the isothermal section by annealing at 800° C. for 1 hr., followed by slow cooling. This slow cooling allowed phases to separate as relatively large particles, easily identified under the microscope. However, in some cases these large particles of phases hindered the attainment of equilibrium at low temperatures; in such cases the samples were either air-cooled from 800° C. to the desired temperature, or quenched to room temperature and reheated to the desired temperature. The periods of annealing used in determining the various isothermal sections were as follows: 2 days at 800° C., 3 days at 700° C., 4 days at 600° C., up to 10 days at 550° C., 13 days at 525° C., and up to 1 month at 500° C. For the 450° C. section, specimens were held for 20 days at 500° C., and then for 10 weeks at 450° C. In an

attempt to establish equilibrium at 400° C. these specimens were then sectioned, and a portion of each was annealed for 1 month at 400° C.

### III.—EXPERIMENTAL RESULTS AND DISCUSSION

#### 1. THE ISOTHERMAL SECTIONS

The isothermal sections at selected temperatures within the range 800°–400° C. are given in Figs. 1–9. The  $\alpha$  phase boundaries are essentially those determined by Dean *et al.*,<sup>9</sup> who, in their investigation of this portion of the diagram, used a larger number of alloys than the present authors. The results now obtained and those of Dean *et al.* are in good agreement. Similarly, the phase boundaries separating regions containing  $\alpha$ -manganese and  $\beta$ -manganese are those suggested by the earlier workers.<sup>9</sup>

##### (a) The 800° C. and 700° C. Isothermal Sections (Figs. 1 and 2)

Manganese increases the compositional range over which the  $\beta$  phase is stable, and decreases the solubility of aluminium in the  $\alpha$  phase. The range of stability of the  $\gamma$  phase was not determined.\*

##### (b) The 600° C. Isothermal Section (Fig. 3)

The extents of the  $\alpha$ ,  $\beta$ , and  $\gamma$  fields are considerably diminished by the separation of manganese. Two binary eutectoid reactions involving  $\beta$  occur:  $\beta \rightleftharpoons (\alpha + \beta\text{-Mn})$  and  $\beta \rightleftharpoons (\gamma + \beta\text{-Mn})$ , respectively, and the three-phase  $(\alpha + \beta + \beta\text{-Mn})$  and  $(\beta + \gamma + \beta\text{-Mn})$  triangles associated with these reactions appear in this section.

##### (c) The 550° C. Isothermal Section (Fig. 4)

The separation of manganese further diminishes the  $\alpha$  field and to a smaller extent the  $\beta$  field. In binary copper-aluminium alloys, the  $\beta \rightleftharpoons (\alpha + \gamma)$  reaction occurs at 565° C. The addition of manganese lowers this temperature, and gives rise to a three-phase  $(\alpha + \beta + \gamma)$  triangle. At 550° C., the composition of  $\beta$  in equilibrium with  $\alpha$  and  $\gamma$  is approximately 1.8% manganese and 11.5% aluminium.

##### (d) The 525° C. Isothermal Section (Fig. 5)

Alloys containing more than approximately 16% manganese and between 5 and 10% aluminium show the existence of a phase absent at higher temperatures. This phase appears to be that designated  $\beta'$  by Dean *et al.*,<sup>9</sup> who, however, did not establish conclusively either its stability or its structure. Over a certain compositional range, the phase replaces both the  $\beta$  and  $\beta$ -manganese in a peritectoid type of reaction; this reaction does not readily proceed to completion.† Two- and three-phase fields containing this phase are present in the isothermal section.

\* The symbol  $\gamma$  refers to both the  $\gamma_1$  and  $\gamma_2$  phases present in binary copper-aluminium alloys, since the effect of manganese on the  $\gamma_1/\gamma_2$  relationship was not determined.

† In determining the isothermal sections at 525° C., and at lower temperatures, a treatment involving slow cooling from 800° C., followed by annealing, did not give equilibrium structures

in certain alloys containing the new phase. The slow cooling from 800° C. allowed the separation of  $\beta$ -manganese and the absorption of this phase at the annealing temperature was extremely slow. Air-cooling, or quenching from 800° C., before annealing facilitated the attainment of equilibrium.



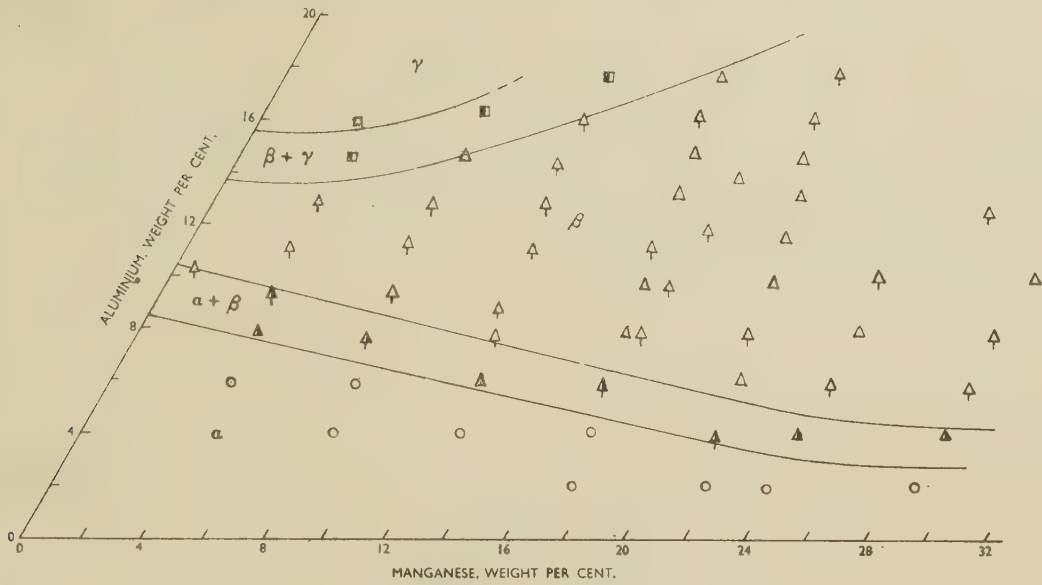


FIG. 1.—The 800° C. Isothermal Section.

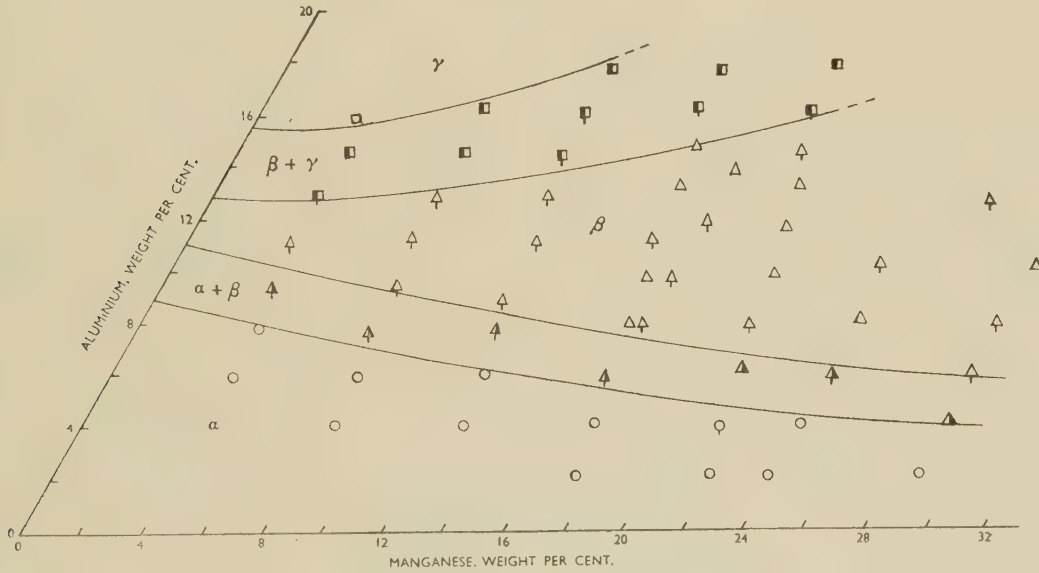


FIG. 2.—The 700° C. Isothermal Section.

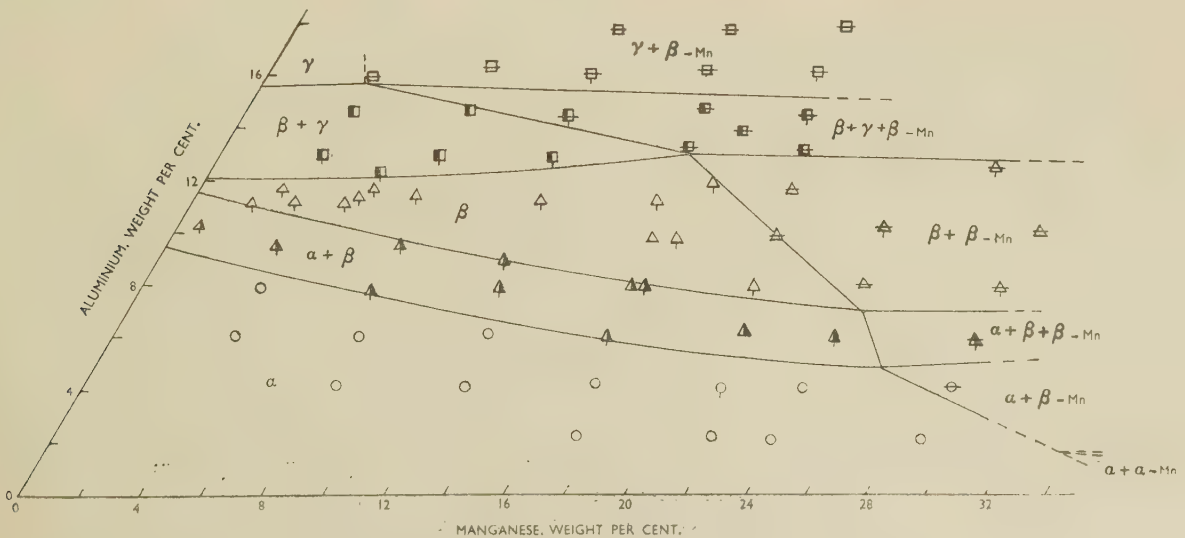


FIG. 3.—The 600° C. Isothermal Section.

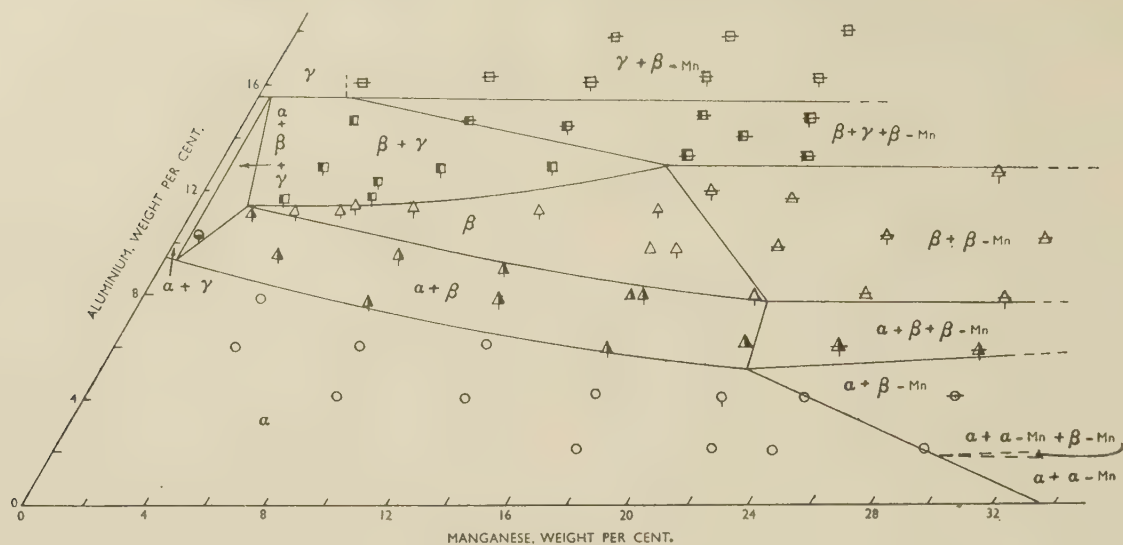


FIG. 4.—The 550° C. Isothermal Section.

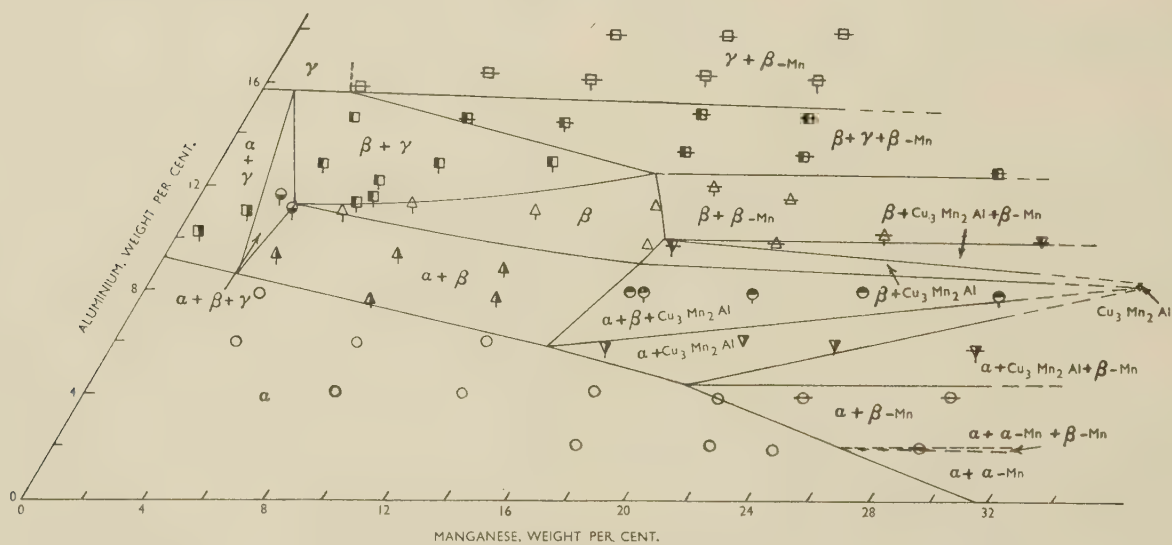


FIG. 5.—The 525° C. Isothermal Section.

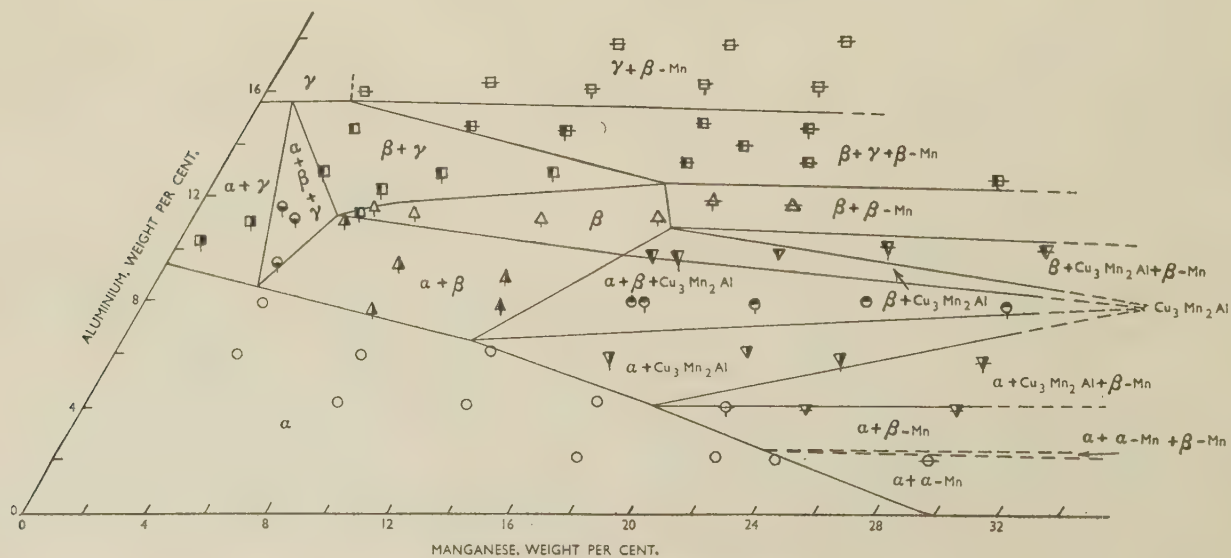


FIG. 6.—The 500° C. Isothermal Section.



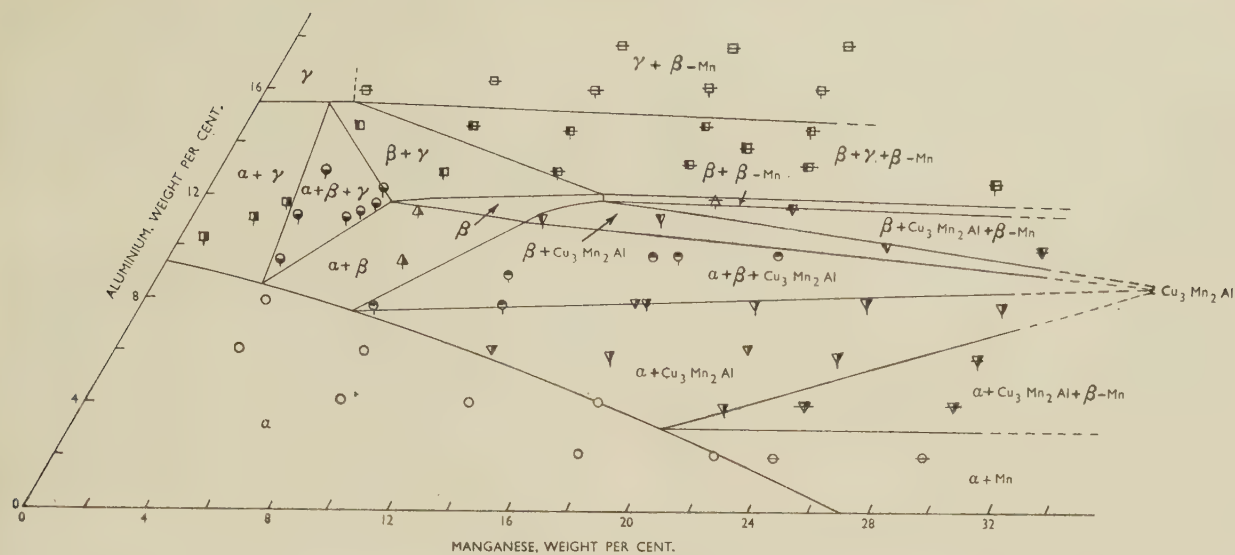


FIG. 7.—The 450° C. Isothermal Section.

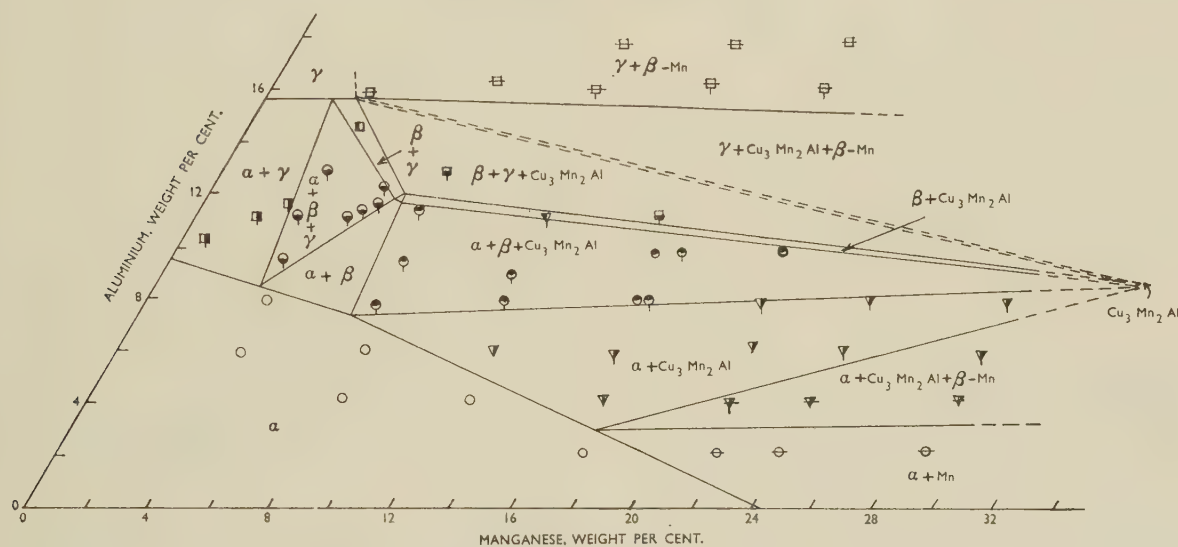


FIG. 8.—The Isothermal Section at Approximately 425° C.

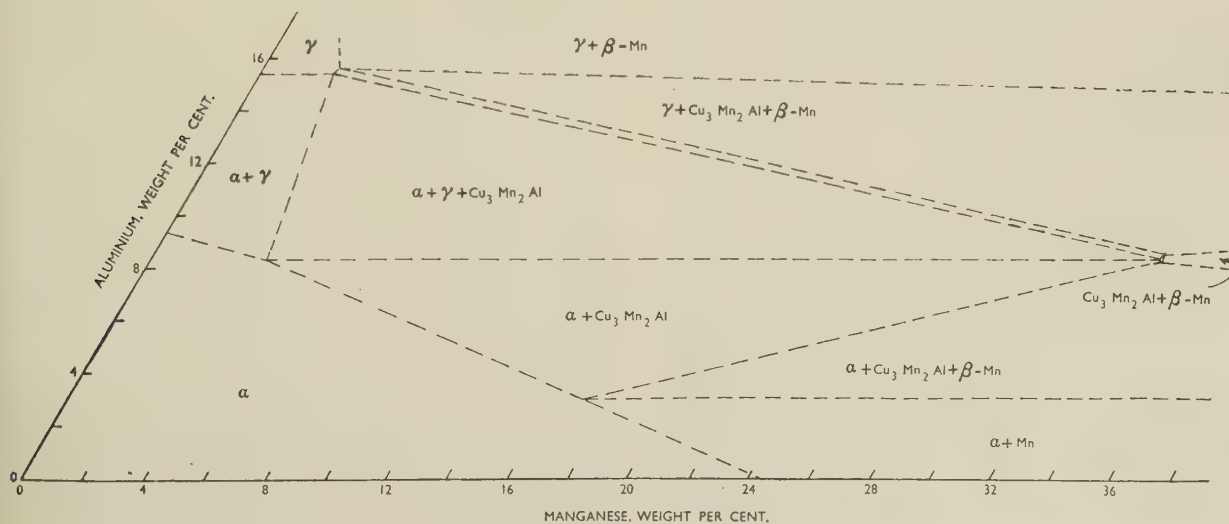


FIG. 9.—The Probable Form of the 400° C. Isothermal Section.

Although a structure consisting entirely of the new phase was not obtained in any of the alloys examined, extrapolation of phase boundaries suggests that a single-phase region is present at approximately 33% manganese and 8% aluminium, corresponding approximately to  $\text{Cu}_3\text{Mn}_2\text{Al}$ . X-ray examination of powder samples containing this phase, co-existing with the  $\alpha$  and  $\beta$  phases, respectively, indicated a face-centred cubic structure with  $a = 6.89$  kX. Calculations based on specific-gravity measurements of samples containing the phase co-existing with  $\alpha$  phase, indicated that the number of atoms per unit cell is 24. Microscopical examination of the phase frequently revealed twin markings, this feature being in accordance with a face-centred cubic structure. The hardness of  $\text{Cu}_3\text{Mn}_2\text{Al}$ , as determined by microhardness measurements, was approximately 500 D.P.N. Fig. 11 (Plate XIX) shows the phase associated with  $\alpha$  and  $\beta$ .

The three-phase ( $\alpha + \beta + \gamma$ ) triangle occurs at slightly higher manganese contents than at  $550^\circ\text{C}$ ., the composition of  $\beta$  in equilibrium with ( $\alpha + \gamma$ ) being approximately 3.5% manganese and 11.4% aluminium.

(e) *The  $500^\circ\text{C}$ . and  $450^\circ\text{C}$ . Isothermal Sections*  
(Figs. 6 and 7)

$\text{Cu}_3\text{Mn}_2\text{Al}$  occurs in alloys of lower manganese contents than at  $525^\circ\text{C}$ . The compositional range over which  $\beta$  is stable decreases considerably by the displacement of the ( $\alpha + \beta + \gamma$ ) and ( $\alpha + \beta + \text{Cu}_3\text{Mn}_2\text{Al}$ ) triangles. Interesting microscopical features develop in some low-manganese alloys containing  $\beta$ , and these are discussed later.

(f) *The  $425^\circ\text{C}$ . and  $400^\circ\text{C}$ . Isothermal Sections*  
(Figs. 8 and 9)

Annealing for 1 month at  $400^\circ\text{C}$ . did not establish equilibrium in all the alloys. It was concluded that the isothermal section constructed from the microstructures of these alloys was representative of a temperature somewhat higher than  $400^\circ\text{C}$ . This section is shown in Fig. 8, and is marked as corresponding to  $425^\circ\text{C}$ . for reasons described below.

The  $\beta$  exists over only a small compositional range. A new three-phase region appears which contains ( $\beta + \gamma + \text{Cu}_3\text{Mn}_2\text{Al}$ ). This results from the eutectoidal decomposition of  $\beta$  to ( $\gamma + \text{Cu}_3\text{Mn}_2\text{Al}$ ), a reaction illustrated in Fig. 12 (Plate XIX), where the eutectoid mixture of ( $\gamma + \text{Cu}_3\text{Mn}_2\text{Al}$ ) is seen growing into  $\beta$  from a large  $\text{Cu}_3\text{Mn}_2\text{Al}$  particle.

A sample containing 3.7% manganese and 9.4% aluminium showed a four-phase ( $\alpha + \beta + \gamma + \text{Cu}_3\text{Mn}_2\text{Al}$ ) structure, indicating a ternary eutectoidal decomposition of the  $\beta$  phase. Selected samples of alloys surrounding the  $\beta$  composition were further annealed for about 2 weeks at  $385^\circ\text{C}$ ., and these gave additional evidence of a ternary eutectoid in which  $\beta$  decomposed into ( $\alpha + \gamma + \text{Cu}_3\text{Mn}_2\text{Al}$ ). Only one of these samples appeared to have attained equilibrium, and this sample was re-treated at  $400^\circ$  and  $420^\circ\text{C}$ . for times of approximately 2 weeks. No significant change in microstructure was noted after treatment at  $400^\circ\text{C}$ ., but appreciable amounts of the  $\beta$  phase reappeared after the  $420^\circ\text{C}$ . treatment. It is considered, therefore, that the temperature of the  $\beta \rightleftharpoons (\alpha + \gamma + \text{Cu}_3\text{Mn}_2\text{Al})$  eutectoid

lies within the approximate limits  $420^\circ$ – $400^\circ\text{C}$ . Fig. 8 thus shows an isothermal section determined after annealing for 1 month at  $400^\circ\text{C}$ ., but, as stated above, it would appear that it more nearly represents equilibrium conditions at about  $425^\circ\text{C}$ ., i.e. slightly above the ternary eutectoid. Fig. 9 indicates the probable form of the isothermal section at  $400^\circ\text{C}$ .

## 2. THE DECOMPOSITION OF THE $\beta$ PHASE

The isothermal sections show that the compositional range of stability of  $\beta$  decreases with falling temperature until, at approximately  $420^\circ$ – $400^\circ\text{C}$ . the  $\beta$  decomposes in a ternary eutectoid reaction. It is of interest to consider the reactions involving  $\beta$  at temperatures above that of the ternary eutectoid. The following account of these reactions is based on a consideration of the phase regions that appear in the isothermal sections (Figs. 1–8) and the reactions are described by reference to the plan view of the  $\beta$  field (Fig. 10).

The occurrence of the binary eutectoid reactions  $\beta \rightleftharpoons (\alpha + \beta\text{-Mn})$  and  $\beta \rightleftharpoons (\gamma + \beta\text{-Mn})$  along the curves  $AB$  and  $CD$  respectively is indicated by three-phase ( $\alpha + \beta + \beta\text{-Mn}$ ) and ( $\beta + \gamma + \beta\text{-Mn}$ ) triangles in the  $600^\circ\text{C}$ . isothermal section (Fig. 3). The ternary phase  $\text{Cu}_3\text{Mn}_2\text{Al}$  forms by a peritectoid reaction:  $(\beta + \beta\text{-Mn}) \rightleftharpoons \text{Cu}_3\text{Mn}_2\text{Al}$ . The composition of  $\beta$  undergoing this reaction is represented by the curve  $BGD$  on which  $G$  is the point of maximum temperature. It may be deduced from the isothermal sections at  $550^\circ$  and  $525^\circ\text{C}$ . (Figs. 4 and 5) that the composition of point  $G$  is, very approximately, 16% manganese and 10% aluminium and the temperature is probably just below  $550^\circ\text{C}$ . The intersection of the binary peritectoid curve  $GB$  with the binary eutectoid curve  $AB$  results in a ternary peritectoid reaction:  $(\beta + \beta\text{-Mn}) \rightleftharpoons (\alpha + \text{Cu}_3\text{Mn}_2\text{Al})$ . From the isothermal sections at  $550^\circ$  and  $525^\circ\text{C}$ . (Figs. 4 and 5) it may be deduced that the composition of the invariant point  $B$  is, very approximately, 17% manganese and 8% aluminium and the temperature between approximately  $550^\circ$  and  $525^\circ\text{C}$ .

Similarly, the intersection of the binary peritectoid curve  $GD$  with the binary eutectoid curve  $CD$  results in the ternary peritectoid reaction:  $(\beta + \beta\text{-Mn}) \rightleftharpoons (\gamma + \text{Cu}_3\text{Mn}_2\text{Al})$ . The isothermal sections at  $450^\circ$  and  $425^\circ\text{C}$ . (Figs. 7 and 8) indicate that the composition of the invariant point  $D$  is, very approximately, 13% manganese and 12% aluminium, and the temperature between approximately  $450^\circ$  and  $425^\circ\text{C}$ .

The binary eutectoid reaction  $\beta \rightleftharpoons (\alpha + \text{Cu}_3\text{Mn}_2\text{Al})$  is represented by the curve  $BE$ , the associated three-phase ( $\alpha + \beta + \text{Cu}_3\text{Mn}_2\text{Al}$ ) triangle appearing in the isothermal sections for temperatures from  $525^\circ$  to  $425^\circ\text{C}$ . (Figs. 5–8). The curve  $DE$  represents the binary eutectoid reaction  $\beta \rightleftharpoons (\gamma + \text{Cu}_3\text{Mn}_2\text{Al})$ , the three-phase ( $\beta + \gamma + \text{Cu}_3\text{Mn}_2\text{Al}$ ) triangle appearing in the  $425^\circ\text{C}$ . isothermal section; and similarly the curve  $FE$  represents the binary eutectoid reaction  $\beta \rightleftharpoons (\alpha + \gamma)$ , the three-phase ( $\alpha + \beta + \gamma$ ) triangle appearing in the isothermal sections for temperatures from  $550^\circ$  to  $425^\circ\text{C}$ . The intersection of the above three binary eutectoid curves,  $BE$ ,  $DE$ , and  $FE$ , results in the ternary eutectoid reaction  $\beta \rightleftharpoons (\alpha + \gamma + \text{Cu}_3\text{Mn}_2\text{Al})$ . The composition of the invariant point  $E$  is approximately 6% manganese



and 12% aluminium, and the temperature lies within the approximate limits 420°–400° C.

### 3. THE ORDERING OF THE $\beta$ PHASE

The  $\beta$  phase in the copper-aluminium system is of disordered body-centred cubic structure, and, under equilibrium conditions, decomposes eutectoidally at 565° C. into the  $\alpha$  and  $\gamma$  phases. When the eutectoid reaction is suppressed by rapid cooling, ordering of the body-centred structure occurs, the ordered form being known as  $\beta_1$ .<sup>12</sup> The change from  $\beta$  to  $\beta_1$  in an alloy containing 12.5% aluminium (i.e. the  $\text{Cu}_3\text{Al}$  composition) would appear to occur at about 550° C. and, in alloys of lower aluminium content, the  $\beta_1$  forms over a range of

alloys containing approximately 11.5% aluminium and up to 20% manganese, and also to an alloy of approximately the  $\text{Cu}_2\text{MnAl}$  composition. With each of these alloys a thermal arrest, believed to correspond to the  $\beta \rightarrow \beta_1$  transformation, was obtained, the temperature of the arrest increasing with the manganese content beyond about 10% manganese; that for the  $\text{Cu}_2\text{MnAl}$  composition was approximately 625° C. The furnace-cooling employed for the thermal analysis suppressed precipitation of phases from  $\beta$  except for a small amount of  $\beta$ -manganese in the high-manganese alloys.

X-ray examination of several alloys was made at temperatures just below those of the cooling-curve arrest points, and superlattice lines were noted. These were absent on similar photographs taken at higher

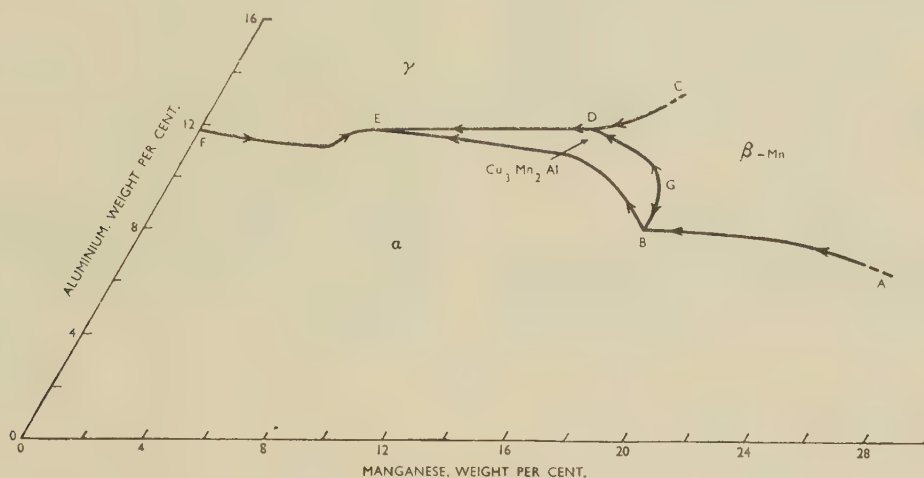


Fig. 10.—A Plan View of the  $\beta$  Field.

Curve	Reaction
AB	$\beta \rightleftharpoons (\alpha + \beta\text{-Mn})$
CD	$\beta \rightleftharpoons (\gamma + \beta\text{-Mn})$
BGD	$(\beta + \beta\text{-Mn}) \rightleftharpoons \text{Cu}_3\text{Mn}_2\text{Al}$
BE	$\beta \rightleftharpoons (\alpha + \text{Cu}_3\text{Mn}_2\text{Al})$
DE	$\beta \rightleftharpoons (\gamma + \text{Cu}_3\text{Mn}_2\text{Al})$
FE	$\beta \rightleftharpoons (\alpha + \gamma)$

KEY TO FIG. 10

Point	Reaction	Temperature (within approximate limits), ° C.	Approximate Composition	
			Mn, %	Al, %
G	$(\beta + \beta\text{-Mn}) \rightleftharpoons \text{Cu}_3\text{Mn}_2\text{Al}$	550–525	16	10
B	$(\beta + \beta\text{-Mn}) \rightleftharpoons (\alpha + \text{Cu}_3\text{Mn}_2\text{Al})$	550–525	17	8
D	$(\beta + \beta\text{-Mn}) \rightleftharpoons (\gamma + \text{Cu}_3\text{Mn}_2\text{Al})$	450–425	13	12
E	$\beta \rightleftharpoons (\alpha + \gamma + \text{Cu}_3\text{Mn}_2\text{Al})$	420–400	6	12

temperature. The metastable  $\beta/\beta_1$  relationship over the compositional range 11–12.5% aluminium has been determined by Thomas.<sup>13</sup> Studies of the isothermal decomposition of the  $\beta$  phase have suggested that  $\beta_1$  in metastable equilibrium with  $\alpha$  is richer in aluminium than would be  $\beta$  in metastable equilibrium with  $\alpha$  at the same temperature. The  $\beta_1 \rightarrow (\alpha + \gamma)$  eutectoid composition is approximately 12.5% aluminium,<sup>14</sup> whereas that of the  $\beta \rightleftharpoons (\alpha + \gamma)$  eutectoid is 11.8% aluminium.

Previous X-ray studies of the quenched  $\beta$  phase in the ternary system have shown it to be body-centred cubic with a face-centred cubic superstructure. The superstructure was reported by Persson<sup>15,16</sup> and by Potter,<sup>17</sup> the position of the aluminium atoms being the same as in the  $\text{Fe}_3\text{Al}$  structure. O. Heusler<sup>18,19</sup> and Bradley and Rodgers<sup>20</sup> determined the positions of the copper and manganese atoms, and found that these also occupied specific positions. The ideal ordered alloy is that corresponding to the  $\text{Cu}_2\text{MnAl}$  composition (viz. 26.3% manganese and 12.9% aluminium).

In order to determine approximately the temperatures at which ordering occurs, thermal analysis was applied to

temperatures. It is concluded that at high temperatures the  $\beta$  structure is disordered body-centred cubic, and this changes to  $\beta_1$  at temperatures from approximately 550° to 625° C., in alloys whose compositions lie on a line between  $\text{Cu}_3\text{Al}$  and  $\text{Cu}_2\text{MnAl}$ . Both binary and ternary alloys containing somewhat less aluminium than those on the  $\text{Cu}_3\text{Al}$ – $\text{Cu}_2\text{MnAl}$  compositional line, appear to order at lower temperatures and over a range of temperature.

The ordering temperatures were not determined over the complete range of composition in which ordering occurs, and the high-temperature X-ray experiments were not used to establish accurately the ordering range. The experimental evidence available is insufficient to plot fully the  $\beta \rightleftharpoons \beta_1$  reaction, and in the isothermal sections and in the discussion of the decomposition of the  $\beta$  phase both  $\beta$  and  $\beta_1$  are designated  $\beta$ .

It is interesting to note, however, that  $\beta_1$ , which is metastable in the copper-aluminium system, becomes stable in the ternary system. The metastable  $(\beta + \beta_1)$  region extending from the copper-aluminium system into the ternary system intersects the  $(\alpha + \beta + \gamma)$

triangle of the  $\beta \rightleftharpoons (\alpha + \gamma)$  reaction in the ternary system. At manganese contents beyond the intersection  $\beta_1$  becomes a stable phase. The transition from  $\beta$  to  $\beta_1$  in this higher-manganese region apparently involves a two-phase region in which  $\beta$  and  $\beta_1$  coexist. An alloy of composition 5.8% manganese and 11.6% aluminium, annealed for periods of up to 1 month at 500° C., showed a  $(\beta + \beta_1)$  structure (Fig. 13, Plate XIX). This is considered to be evidence for the existence of a stable  $(\beta + \beta_1)$  region in the ternary system. As stated above, this region is not shown in the isothermal section.

The formation of  $\beta_1$  produces a displacement of some phase boundaries to slightly higher aluminium contents. Thus, the aluminium content of  $\beta$  in equilibrium with  $(\alpha + \gamma)$  decreases from 11.8% at 565° C. to approximately 11.2% at 500° C., but at 450° C.  $\beta_1$  containing approximately 11.8% aluminium is in equilibrium with  $(\alpha + \gamma)$ . Curve *FE* in Fig. 10 illustrates this. Similarly, the structure of an alloy containing 5.8% manganese and 11.6% aluminium at 525° C. consists of  $(\gamma + \beta)$ ; at 500° C. it is  $(\beta + \beta_1)$ , and at 475° C. it is  $(\alpha + \beta_1)$ .

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# THE HARDNESS OF MANGANESE AND SOME MANGANESE-RICH ALLOYS \*

1728

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## SYNOPSIS

Diamond-pyramid hardness tests on electrolytic manganese and some of its dilute alloys have shown that  $\alpha$ -manganese is about ten times as hard as the  $\gamma$  phase. This ratio is of the same order as that between the hardness of various electron compounds and the average hardness of their component metals—an observation consistent with the view of Bradley and Thewlis (*Proc. Roy. Soc.*, 1927, [A], 115, 456) that  $\alpha$ -manganese is constitutionally more like an electron compound than a typical metal. The hardness values of some quenched  $\gamma$  alloys of manganese with copper and nickel, after various reheating treatments, are given.

## I.—INTRODUCTION

A CONSIDERABLE amount of quantitative information is available regarding the effect of alloying and of cold work on the hardness of metals. The influence of complicated crystal structure, however, especially in pure metals, has not yet received much detailed attention, and manganese presents points of interest in this connection. Four allotropic modifications, possessing a wide range of mechanical properties, are known, and particulars of them are given in Table I.

## II.—EXPERIMENTAL TECHNIQUE AND RESULTS

### 1. HARDNESS OF ELECTRON COMPOUNDS

Four representative alloys were cast from commercial metals and their Vickers hardness numbers determined. In some cases the values are not highly accurate, as slight cracks appeared round the indentations in the brittle alloy.

TABLE II.—*Hardness of Electron Compounds in Relation to Components.*

TABLE I.—*Allotropic Modifications of Manganese.*<sup>1-3</sup>

Form	Transition Temp., °C.	Lattice Type and Atoms/Unit Cell	Interatomic Distance, Å.	Properties
$\alpha$	700 (sluggish)	b.c.c. (58 atoms)	2.24–2.95	Very hard and brittle. Rockwell C71
$\beta$	1100	Cubic as quenched (20 or possibly 160 atoms)	2.365–2.675	Very hard as quenched
$\gamma$	1133	f.c.c. at high temp. (4 atoms) f.c. tetragonal at room temp. (4 atoms)	...	Soft and ductile Rockwell C23
$\delta$	Melts at 1244° C.	b.c.c. at high temp. Cannot be retained ...	...	...

Electron Compound	Crystal Structure	Vickers Pyramid Hardness No. (10-kg. load)		
		Average of Components	Alloy	Increase
Mg <sub>17</sub> Al <sub>12</sub>	Like $\alpha$ -Mn	38; 30 = 34	200	6-fold
Cd <sub>8</sub> Cu <sub>5</sub>	" "	20; 43 = 31	300	10 "
Cu <sub>2</sub> Zn <sub>8</sub>	" "	43; 60 = 51	430	8.5 "
Ag <sub>3</sub> Al	" $\beta$ -Mn	40; 30 = 35	220	6 "

The results given in Table II show that the brittle compounds have a hardness of 6–10 times that of their ductile components. A similar ratio might therefore be expected for the hard and soft forms of manganese.

Whilst  $\beta$ -manganese can be retained at room temperature by quenching from above the  $\alpha \rightarrow \beta$  transformation, this does not apply to the  $\gamma$  and  $\delta$  forms, as these tend to revert to  $\alpha$ . Hardness determinations were attempted by (a) testing at elevated temperatures with the possibility of extrapolating back, and (b) quenching dilute alloys to preserve high-temperature phases.

### 2. HIGH-TEMPERATURE TESTS

Bens<sup>5</sup> has designed an apparatus, using the standard Vickers diamond mounted in copper-nickel alloy, which worked satisfactorily up to 850° C. Apparatus basically similar to that of Bens, but 2 in. smaller in overall dimensions, was kindly made available for the present investigation by Mr. A. S. Kenneford. This is shown in Fig. 1. It was operated under an atmosphere of hydrogen.

Bradley and Thewlis<sup>4</sup> have suggested that in  $\alpha$ -manganese the electrons are not equally shared between the different atoms in the structure, so that the phase behaves more like an electron compound than a true element. This led the present authors to undertake a preliminary study of the hardness of certain electron compounds in relation to that of their component elements.

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A diamond indenter with a special high-temperature mount was obtained from Messrs. Vickers-Armstrongs; this showed no pronounced deterioration after use up to 1180° C. The specimen was traversed on the anvil for indenting at appropriate temperatures by means of the adjusting screw, and the indentations were afterwards measured at room temperature. As there was no flexible connection between the loading piston of the Vickers machine and the top of the indenter extension rod, it was necessary to position the tester by trial and error, and small differences in friction may have been the cause of unavoidable scatter in the results.

A piece of 99.9% electrolytic manganese, after de-oxidation in hydrogen,<sup>6</sup> was set in a small steel block by means of a cement of alumina and water-glass, polished on 0 emery paper, and placed in position in the apparatus. Purified hydrogen was next passed through for at least

denly drops to about 18 as  $\beta$  is formed. At high temperatures the graphs are not sufficiently accurate to permit extrapolation to room temperature for estimation of the relative hardness of the phases. The indication is that  $\beta$  would be softer than  $\alpha$ , and this is supported by the fact that its atomic volume and electrical resistivity are intermediate between those of  $\alpha$  and  $\gamma$ , but the unknown effect of hydrogen has also to be considered. Decreasing solubility in the  $\alpha$  range gives place to a marked absorption on transformation to  $\beta$ , followed by an increase of solubility with temperature.

### 3. PREPARATION AND HEAT-TREATMENT OF MANGANESE ALLOYS

Alloys of manganese with small amounts of another metal were prepared, so that the  $\gamma$  phase might be re-

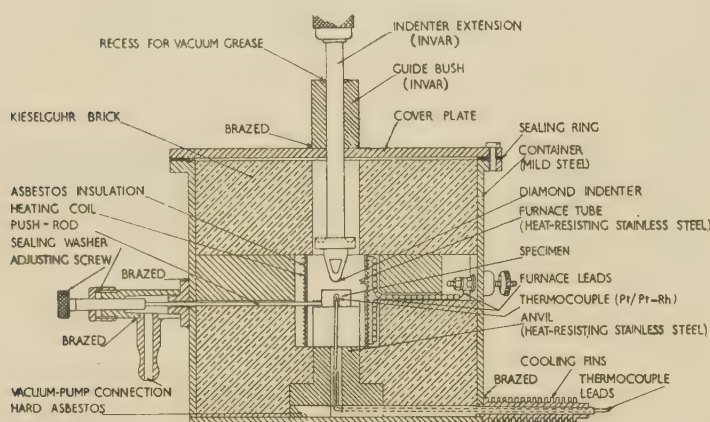


FIG. 1.—Hardness Tester for High Temperatures.

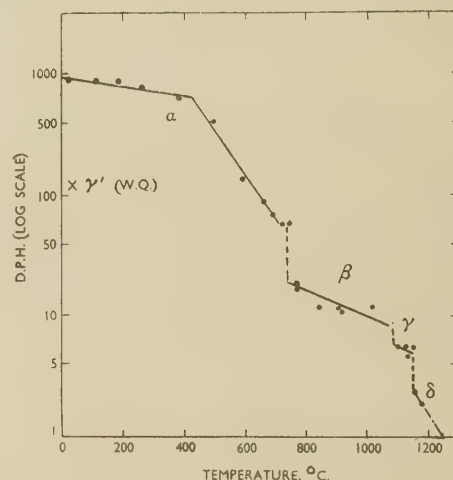


FIG. 2.—Vickers Hardness Measurements on Electrolytic Manganese Made at Increasing Temperature up to 1175° C. under Hydrogen.

4 hr. before heating. Hydrogen was then supplied as fast as the purification train would permit, since the specimen was very liable to oxidize. Temperatures were read by a potentiometric thermocouple system during the time (15 sec.) that an indentation was being made. A load of 10 kg. was used up to 600° C., 5 kg. from 600° to 800° C., and 1 kg. from 800° to 1180° C. Tests with this last load are not likely to be very accurate.

A number of specimens were thus indented in hydrogen at a series of rising temperatures, and the mean results are plotted semi-logarithmically in Fig. 2. The log of the hardness was used because Westbrook<sup>7</sup> had found that it bore a linear relationship to temperature for pure metals. His graphs gave a change of slope at about 0.55 of the absolute melting point, and Fig. 2 shows a similar inflection for  $\alpha$ -manganese at about 450° C. (0.48 of the absolute melting point). This inflection is not fully understood, but it has been suggested that effects due to stress-relief or viscous flow eventually predominate over the ordinary slip process prevailing at the lower temperatures. It should be emphasized that the present results and also those of Westbrook are for constant times of indentation loading.

Fig. 2 gives evidence of the allotropic changes. The hardness of  $\alpha$ , which is 58 V.P.N. at about 700° C., sud-

tained at room temperature by quenching. Electrolytic manganese (99.9%) was first given a slow heating *in vacuo* to 500° C. and held for 1 hr., after which it was heated in carefully purified hydrogen at 850°–900° C. for 18 hr. Alloying elements were chemically cleaned and dried and weighed out to give 60–80-g. melts, allowing for about 1% loss of manganese. The copper and aluminium used were of 99.9% purity, whilst the nickel was 99.98% and the chromium 99.99% pure.

The metals were placed in a small recrystallized alumina crucible which was contained in a larger one before introduction into the fused-quartz tube of a high-frequency melting furnace. After the vacuum pumps had been run for 1–2 hr., the furnace was operated at low power until the Pirani gauge showed degassing to be almost complete. Purified argon was then introduced up to atmospheric pressure, and the power increased so as to bring about melting in 20–30 min.

For quenching treatment, pieces of alloy were suspended in a vertical Silit furnace. Sometimes they were coated with a thin protective layer of alumina and carried in a nickel-foil basket, or alternatively they were fixed in a small piece of alumina tubing. The atmosphere was purified argon, and after soaking at temperature for 2 hr. the specimens were water-quenched.



A specimen of a nominal nickel content of 5%, kindly prepared by The Mond Nickel Co., Ltd., for earlier work,<sup>8</sup> was also tested.

#### 4. HARDNESS OF THE VARIOUS PHASES

The hard phases of manganese are so brittle that cracks are liable to form round pyramid indentations. These cracks probably spring apart under the testing load, and the results measured from such unloaded indentations are therefore liable to be higher than the true ones. A few results obtained with a Bergsman microtester have been included with the Vickers values in Table III.

It should be pointed out that a diagonal measurement error of 0.001 mm. at 950 V.P.N. (10-kg. load) corresponds to 14 units of hardness.

TABLE III.—Hardness-Testing Results on Manganese Alloys.

Alloying Element, %	Heat-Treatment	V.P.N. (10-kg. load)	Bergsman Hardness No. (300-g. load)	Phases Present
Manganese	Coarse crystals	974	916	$\alpha$
2.8 Ni	W.Q. from 1180° C.	(high)	...	...
6 Cr (nominal)	" 1180° C.	(high)	...	...
4.9 Cu	Annealed at 650° C. for 5 weeks	...	955	$\alpha$ + feathery constituent $\alpha$ + finely dispersed $\gamma$
Manganese	W.Q. from 1000° C., fine crystals	966	991	$\beta$
10 Al (nominal)	W.Q. from 1050° C.	(high)	802	$\beta$
	" 1200° C.	...	823	$\beta$
	Annealed at 650° C. for 5 weeks	...	881	$\beta$
3.1 Ni	W.Q. from 1100° C.	152	...	$\gamma$
5.2 Ni	" 1180° C.	155	...	...
5.2 Ni	" 1180° C.	135	...	...
0.15 C, 0.05 Si	" 1100° C., reheated to 910° C., and W.Q.	107	...	$\gamma$
4.9 Cu		210	210	$\gamma + \beta$

W.Q. = water-quenched.

Dr. Marie Gayler kindly provided some of her original (1929) thermal-analysis specimens of vacuum-distilled manganese, and these were tested as received by one of the present authors [H. O'N.] with the Vickers machine and with the Zeiss Hanemann microtester of the Bragg Laboratory, Sheffield. The latter is known<sup>9</sup> to give values higher than the former to the extent of about 280 on a hard steel of about 800 kg./mm.<sup>2</sup>. This correction has therefore been deducted, giving the following results:

Hanemann test (100-g. load) . . . . . 1345 — 280 = 1065  
Vickers test (5-kg. load) . . . . . 1042

It appears that this metal is harder than the material used in the present work, but the microstructure was not homogeneous, and it may have contained some  $\beta$  phase. Tests carried out by Mr. B. W. Mott with the Vickers pyramid at 100 g. on a Tukon tester at the Atomic Energy Research Establishment, Harwell, gave 1003 kg./mm.<sup>2</sup> on the matrix and 721 kg./mm.<sup>2</sup> on the constituent at the grain boundaries.

It may be concluded that the quenched  $\gamma$  phase has a Vickers hardness of about 100 kg./mm.<sup>2</sup>, if a deduction is made for alloying, whilst the  $\alpha$  phase reaches about 950 kg./mm.<sup>2</sup>. The  $\beta$  phase after quenching gives about the same hardness as  $\alpha$ . The ratio between the hard and

soft forms is about 9 to 1, corresponding roughly with that for the electron compounds in Table II.

#### 5. THE REHEATING OF QUENCHED ALLOYS

A short study was made of the hardening of the soft quenched alloys as the  $\gamma$  phase partially transformed. Reheating to 500° C. was carried out in electric muffles in air, as this duplicated results on some test specimens tempered *in vacuo*. From 500° to 800° C., the alloys were reheated *in vacuo*, but above this temperature specimens were sealed in alumina-lined silica-glass tubes containing argon to hinder volatilization. All specimens were water-quenched after reheating for 7 days, the tubes being simultaneously broken. Coles and Hume-Rothery<sup>2</sup> annealed their manganese-nickel alloys for 4 days at 1000° and 7 weeks at 600° C. (though they suggest that "equilibrium is soon established"), so that the present work shows only general tendencies.

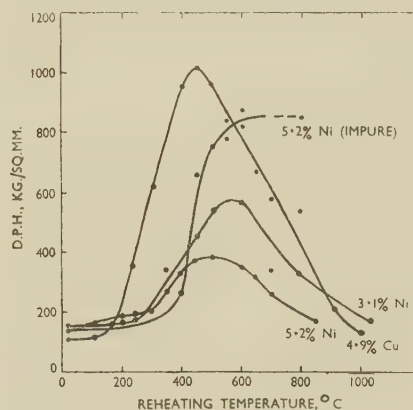


FIG. 3.—Vickers Hardness Measurements on Quenched Alloys Containing the  $\gamma$ -Manganese Phase After Reheating to Various Temperatures.

The reheated alloys were mounted and given a metallographic preparation before hardness testing. A separate specimen was used for each reheating temperature, and the Vickers values are given in Fig. 3. As the hardness reached 400–500 kg./mm.<sup>2</sup> the indentations began to show cracks, and when large particles of a second phase formed, the results were variable and average values are given.

#### 6. METALLOGRAPHY

The specimens were all small, irregular, and generally cracked. They were mounted in cold-setting Bakelite or in Bakelite at 120°–140° C., and a cement was used to hold very brittle and badly cracked specimens in the mount. No differences were found between these two mounting materials, and there were no signs of spontaneous changes after standing for a few weeks.

Etching and drying were very difficult, and no one reagent was wholly satisfactory for all the alloys. The following solutions were found to give good results:

Alloy	Reagent
Mn, Mn-Al, Mn-Cr	6% nitric acid in methyl alcohol.
Mn-Ni	1% ammonium persulphate plus a few drops of acetic acid.
Mn-Cu	1% ammonium persulphate plus a few drops of oxalic acid.

The etching reagent was washed off for a few sec. in running water, and the specimen dried with hot alcohol and a current of warm air. Typical structures are shown in Figs. 4-11 (Plate XX). In spite of the precautions taken, the alloys show inclusions of oxide.

X-ray spectra were obtained, using a 9-cm. Unicam camera with  $\text{MoK}_\alpha$  radiation and a 4-hr. exposure at 50 kV. and 10 m.amp. Cr radiation was not available at the time. Hard specimens were powdered in an agate mortar, and filings were obtained from the softer alloys. The powders were held in tubes of cellulose nitrate formed round 26 S.W.G. copper wires.

### III.—DISCUSSION OF THE RESULTS

Alloys of manganese with 6% chromium or 10% aluminium, or not more than 2.8% nickel, did not soften when quenched from the  $\gamma$  or  $\delta$  fields, but contained  $\alpha$  phase in the chromium alloy and  $\beta$  phase in the others. The quenched copper and higher-nickel alloys gave  $\gamma$  phase showing normal twins and the usual multiple banding caused in manganese by quenching. The quenched alloys after reheating and quenching showed banding in the  $\gamma$  areas.

The metallography of the alloys is difficult owing to the extreme hardness and brittle nature of both  $\alpha$ - and  $\beta$ -manganese. Some specimens were found to be apparently three-phase, and X-rays corroborated this observation. Fig. 11 (Plate XX) shows one such example. Here the black regions are  $\alpha$  phase, the whiter parts are  $\beta$  phase, and the matrix is  $\gamma$  phase. Evidently, reactions in manganese alloys at low temperatures can be very sluggish, and the reheating times used did not establish equilibrium below about 700°–800° C. Consequently, the phase diagram of Kurnakov and Troneva<sup>10</sup> is open to suspicion, as they used annealing times of only 5 days. The phase diagram of Coles and Hume-Rothery<sup>2</sup> was determined after much longer annealing times at the lower temperatures and is more likely to be correct.

Figs. 6-10 (Plate XX) show the structures observed in the quenched 3.1% nickel alloy after reheating at 250°, 400°, 500°, 600°, and 800° C. The  $\gamma$  phase is characterized by multiple banding, and although it is not visible (at least at 250 $\times$ ) in Figs. 7 and 8, it reappears in Figs. 9 and 10. It is interesting to note that the structure shown in Figs. 7 and 8 corresponds to the reheating temperatures where the hardness peak was found.

It proved impossible to distinguish clearly between the  $\alpha$  and  $\beta$  phases by metallographic observation, and X-ray evidence was needed to confirm whether  $\alpha$  or  $\beta$  was present. As Fig. 9 ( $\alpha + \gamma$ ) and Fig. 10 ( $\beta + \gamma$ ) show, the  $\alpha$  and  $\beta$  phases are very similar in appearance. The eventual fall in hardness is due to the homogeneous  $\gamma$  field being approached at higher reheating temperatures, resulting in the preservation of increasing amounts of this soft phase.

The impure 5.2% nickel alloy did not soften on reheating to 800° C. It also appears to have a higher  $\gamma$ -boundary temperature, for it could not consistently be softened by quenching from 1180° C.

The quenched  $\gamma$  phase containing copper was softer than that containing nickel. Apart from impurities, this may be due to the smaller nickel atom causing greater lattice distortion. The copper alloy gave a higher maximum hardness after reheating than did the nickel alloys, and its transformation product was structurally finer. Moreover, the phase diagram suggests that for equal amounts of the two elements, there would be more hard  $\alpha$  present in the copper alloy.

### IV.—CONCLUSIONS

(1) The diamond-pyramid hardness of  $\alpha$ -manganese is about 950 kg./mm.<sup>2</sup>, whilst that of the  $\gamma$  phase at room temperature is about 100 kg./mm.<sup>2</sup>. This 9-fold ratio is about the same as that found between electron compounds (e.g.  $\gamma$ -brass) and their ductile constituents.

(2) Hot hardness tests show breaks at the transformation temperatures and suggest that  $\beta$ -manganese is softer than  $\alpha$ , though quenched  $\beta$  gives values of about 1000 kg./mm.<sup>2</sup> and cracks more severely than  $\alpha$ .

(3) The decomposition of the  $\gamma$  phase by reheating (7 days) and quenching of nickel or copper alloys shows considerable hardening produced by the precipitation of the harder phases. The hardness is a maximum after reheating to about 500° C.

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# LATTICE SPACINGS OF THE SILVER-RICH SOLID SOLUTION CONTAINING MAGNESIUM AND ANTIMONY\*

1729

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## SYNOPSIS

Measurements of the lattice spacings of silver-rich solid solutions containing magnesium and antimony are reported. The silver-rich solid solution comes into equilibrium with three compound phases: (i) the silver-antimony electron compound, (ii) the ternary compound  $\text{AgMgSb}$ , and (iii) the binary compound  $\text{Mg}_3\text{Sb}_2$ . The strictly additive effect of the two solute elements upon the lattice spacing of the ternary solid solution, together with the more extensive solubility, suggests that the extension of electrochemical effects into the solid solution is much less marked for this system than for the previously examined system aluminium-magnesium-silicon. Atom-size considerations are also discussed.

## I.—INTRODUCTION

LATTICE-SPACING relationships in the aluminium-rich ternary solid solutions of the systems aluminium-magnesium-copper<sup>1</sup> and aluminium-magnesium-silicon<sup>2</sup> have already been published. The present paper reports an extension of such investigations to the silver-rich ternary solid solution containing magnesium and antimony. In the course of the work on ternary alloys, a check was made on the lattice spacing of pure silver and also on the accepted lattice-spacing relationships for the silver-rich binary solid solutions of the systems silver-magnesium<sup>3</sup> and silver-antimony.<sup>4</sup>

## II.—EXPERIMENTAL METHODS

### 1. METALS USED

The silver was pure assay silver supplied in globular form by Messrs. Johnson, Matthey and Co., Ltd., the purity being not less than 99.95%. The magnesium was from the same batch of "Specpure" material as that used in the previous investigations.<sup>1,2</sup> The antimony was supplied in the form of broken ingots by Messrs. Johnson, Matthey and Co., Ltd., who stated the chemically determined impurities to be lead 0.16, silicon 0.02, nickel 0.004, iron 0.008, arsenic 0.002, and bismuth 0.0002%.

Silver-rich master alloys were prepared by melting the pure elements together in graphite crucibles in an induction furnace. The molten master alloys were cast into cylindrical chill moulds. The ingots were sawn down the central axis and the resulting macrosections were carefully examined for metallographic evidence of segregation. The silver-antimony ingot was found to be completely eutectic in type of structure and was accepted as satisfactory, but the first attempt to produce a silver-magnesium ingot showed a few patches of unmelted silver in the prepared section. This silver-magnesium ingot

was carefully cleaned, remelted quickly, and recast. On subsequent sectioning, the ingot was found to be homogeneous. The saw fettings obtained from the silver-antimony and from the second of the silver-magnesium ingots were analysed, with the following results: silver-antimony: silver 55.10, antimony 44.93, total 100.03%; silver-magnesium: silver 92.13, magnesium 7.85, total 99.98%.

### 2. PREPARATION AND HEAT-TREATMENT OF THE INGOTS

Accurately weighed portions of silver and of the master alloys were melted together in a small graphite crucible, contained within an evacuated silica capsule. The crucibles were made from pure graphite spectrograph electrodes and were large enough to hold about 5 g. of molten silver. Melting was conducted in a high-frequency induction furnace, and rapid solidification of the melt was obtained by quenching the capsules into cold water. The silica capsules did not crack as a result of this treatment, and the alloys solidified in the crucibles to give ingots weighing 2 g. and having a fine grain-size, which facilitated the attainment of equilibrium on annealing.

The alloys were initially annealed for 14 days at 450° C. in evacuated glass capsules, the ingots being protected from contact with the glass by graphite collars. When these specimens were quenched and examined metallographically, some were found to contain traces of a second phase. Hence all specimens were cold worked and re-annealed for a further period of 7 days at 550° C. On re-examination, all the ingots were found to be single-phase and were judged suitable for the production of X-ray filings.

### 3. HEAT-TREATMENT OF FILINGS AND LATTICE-SPACING MEASUREMENTS

The surface layer of each ingot was filed away to a depth of about 1 mm., and this material was rejected as

\* Manuscript received 13 April 1956.

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Electric Co., Ltd., Erith, Kent.

‡ University of Manchester.

being likely to have lost volatile elements during the lump anneal. About 1 g. of filings was prepared from the inner part of each ingot, care being taken to avoid contamination during the process. The filings were passed under a magnet to remove traces of ferro-magnetic material and then washed in ether to remove dust. The filings were contained in graphite collars fitted with end-plates of silver foil held in place by a loop of silver wire. The collars were contained within evacuated capsules of Pyrex glass, and the whole assembly was annealed for 1 hr. at 550° C. At the end of the anneal, the capsules were quenched into cold water, whereon the capsules broke and the water came into immediate contact with the filings. The filings were then washed, dried, and sieved through copper gauze of 60 meshes to the linear inch to remove splinters of broken glass and coarse particles of metal. Of the filings that passed through the sieve, a portion was made up into an X-ray specimen and the remainder subjected to chemical analysis by Messrs. Johnson, Matthey and Co., Ltd. Unfiltered CuK radiation was obtained from a Metropolitan-Vickers "Ray-max" unit, and a 19-cm.-dia. Debye-Scherrer camera made by Unicam Instruments, Ltd., as modified by Poole and Axon,<sup>1</sup> was used. Care was taken to measure the true temperature of the specimen during the X-ray exposure,<sup>5</sup> and this temperature was maintained constant to within 0.5° C. Those films which were of good quality were measured on a Cambridge Universal Measuring Machine, and the lattice spacings were calculated by standard methods, using the tables of Edwards, Lipson, and Wilson<sup>6</sup> and the extrapolation function of Nelson and Riley.<sup>7</sup> All lattice spacings were corrected to a temperature of 25° C., using a value of  $19.0 \times 10^{-6}$  for the coefficient of expansion of silver and its solid-solution alloys. The final values for the lattice spacing at 25° C. were obtained in kX units and depend upon the values 1.537395 for CuK $\alpha_1$  and 1.541232 for CuK $\alpha_2$ . No correction was made for refraction.

### III.—EXPERIMENTAL RESULTS AND DISCUSSION

#### 1. PURE SILVER

The mean value of four experimental determinations of the lattice spacing of the pure silver used in the present work was 4.0777(5) kX at 25° C. It was considered desirable to determine whether the alloys picked up any impurity in the process of casting and lump annealing, and a check on this was made by measuring the lattice spacing of filings taken direct from the silver in the as-received condition and also of filings made from two ingots of silver which had been prepared by melting the metal in a clean graphite crucible and subsequently annealing the ingots in graphite collars. The conditions of melting and lump annealing of the silver ingots were identical with those employed for the preparation of the alloys. No significant difference of lattice spacing was detected between the filings from the as-received globules and those from the ingots. The silver filings were subjected to the same annealing and quenching treatment as were the alloy filings. The present value for the lattice spacing of silver is in reasonable agreement with the values of 4.0778 kX obtained by Andrews and Hume-Rothery<sup>3</sup> for material of 99.99% purity, and of 4.07791

kX obtained by Hume-Rothery, Lewin, and Reynolds<sup>4</sup> for "chemically pure" silver.

#### 2. SILVER-ANTIMONY ALLOYS

The silver-antimony<sup>8</sup> system is characterized by a silver-rich solid solution with a maximum alloy content of 7.2 at.-% at the solidus; the solid-solubility limit appears to decrease linearly with decreasing temperature to a value of about 6.5 at.-% at 550° C. The silver-rich solid solution is in equilibrium with a hexagonal 3/2 electron compound. The lattice-spacing relationship in the silver-antimony solid solution has been investigated by Hume-Rothery, Lewin, and Reynolds,<sup>4</sup> who examined six alloys containing up to 4 at.-% antimony, and also by Owen and Roberts,<sup>9</sup> who examined alloys containing

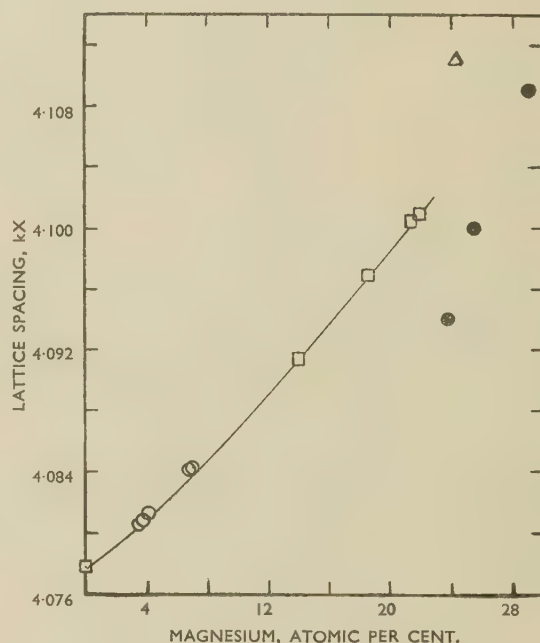


FIG. 1.—Lattice Spacing/Composition Relationship for the Silver-Rich Silver-Magnesium Solid Solution.

KEY  
 ○ Andrews and Hume-Rothery.<sup>3</sup>    △ Clarebrough and Nicholas.<sup>11</sup>  
 ● Letner and Sidhu.<sup>10</sup>    □ Present work.

up to 6.15 at.-% antimony. The results of both investigations are in close agreement; indeed, if the two sets of results are re-calculated to a temperature of 25° C., with no correction for refraction, they can both be represented by the same linear variation of lattice spacing with composition. In the course of the present work, a single binary alloy containing 5.07 at.-% antimony was examined, and, with a lattice spacing of 4.10779 kX, was found to lie upon the same straight line, which was therefore accepted as the best description of the lattice-spacing relationship in the binary silver-antimony system.

#### 3. SILVER-MAGNESIUM ALLOYS

The silver-magnesium<sup>3</sup> system shows an extensive silver-rich solid solution, the maximum solid-solubility limit being placed at 29.3 at.-% at 759° C., falling to 26.5 at.-% at 300° C. The silver-rich solid solution is in equilibrium with an electron compound of the 3/2 type,



having an ordered caesium-chloride structure and a pronounced maximum in the liquidus at the composition AgMg. The lattice spacings of alloys in the solid-solution range have been investigated by several groups of workers, of whom Hume-Rothery and Andrews<sup>3</sup> examined the composition range 0–7 at.-% magnesium, Letner and Sidhu<sup>10</sup> examined three alloys in the range 24–29 at.-% magnesium, and Clarebrough and Nicholas<sup>11</sup> examined an alloy containing 24.3 at.-% magnesium. The results of Andrews and Hume-Rothery may be represented by a reasonably linear lattice spacing against composition relationship, but if this relationship is extended beyond the composition limits examined by Andrews and Hume-Rothery, it is found that the results of the other two groups of workers lie well away from it. Indeed, the results from the three groups of workers are inconsistent, although a study of the original literature suggests that the most reliable results are those of Andrews and Hume-Rothery. In an attempt to resolve this discrepancy between the results of previous workers, a series of four alloys was prepared with compositions 13.93, 18.4, 21.24, and 21.93 at.-% magnesium. The lattice-spacing results for these binary alloys are plotted, together with the results of previous investigators, in Fig. 1, from which it can be seen that the present results confirm the relationship obtained by Andrews and Hume-Rothery.

#### 4. SILVER-MAGNESIUM-ANTIMONY ALLOYS

The binary magnesium-antimony<sup>12</sup> system consists of two eutectics separated by the intermetallic compound  $\text{Mg}_3\text{Sb}_2$ , which melts at 1228° C. and undergoes a polymorphic transformation between 894° and 930° C. The low-temperature form of  $\text{Mg}_3\text{Sb}_2$  is trigonal and anti-isomorphous with  $\text{La}_2\text{O}_3$ .

The 550° C. isothermal of the ternary system has been determined for the silver-rich alloys by Frost and Raynor,<sup>13</sup> who have shown that the silver-rich ternary solid solution comes into equilibrium with the silver-antimony electron compound in the high-antimony, low-magnesium limits of the solid solution, with the binary compound  $\text{Mg}_3\text{Sb}_2$  in the high-magnesium, low-antimony limits of solid solubility, and with the ternary compound  $\text{AgMgSb}$  in the intermediate range. Where the solid solution is in equilibrium with the electron compound, the  $\alpha$  phase boundary tends to be a line of constant electron concentration, but is controlled by relations of the type  $[\text{Mg}][\text{Sb}] = K_1$  and  $[\text{Mg}]^3[\text{Sb}]^2 = K_2$ , when the solid solution is in equilibrium with the compounds  $\text{AgMgSb}$  and  $\text{Mg}_3\text{Sb}_2$  respectively.

The range of solid solubility in the ternary alloys is such that all alloys with compositions on or below the line joining 18 at.-% magnesium to 6 at.-% antimony are completely single-phase at 550° C. The analysed compositions of all the ternary alloys lie near to one of the three lines which, in the ternary system, join 5.0 at.-% antimony to 15.0 at.-% magnesium; 5.67 at.-% antimony to 17.0 at.-% magnesium; or 6.4 at.-% antimony to 12.2 at.-% magnesium, respectively. Alloys which lie near to, but not exactly on, one of these lines may be brought on to the line with an appropriate correction to the observed lattice spacing to allow for the change of composition, as previously described by Poole and Axon. The corrected observations are plotted in Figs. 2 (a)–(c),

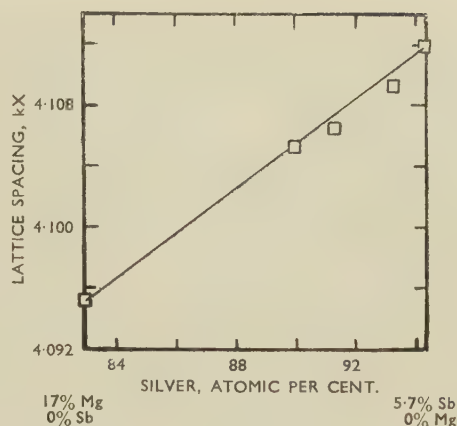


FIG. 2 (a)

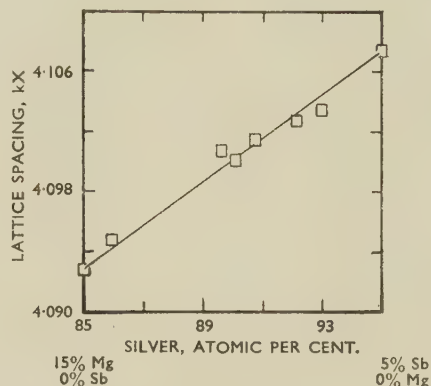


FIG. 2 (b)

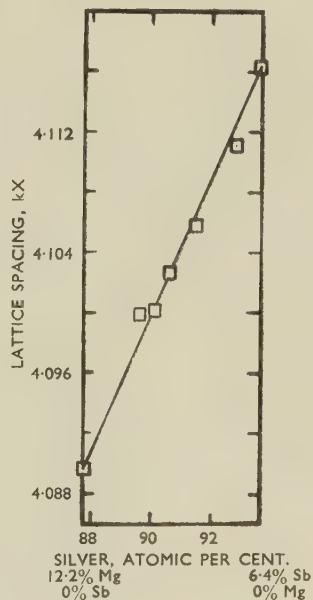


FIG. 2 (c)

FIG. 2.—Lattice Spacings in the Silver-Rich Ternary Solid Solution Containing Magnesium and Antimony. (a) The relationship on the line joining the binary point Mg 17, Sb 0, Ag 83% to the binary point Mg 0, Sb 5.7, Ag 94.3%. (b) The relationship on the line joining the binary point Mg 15, Sb 0, Ag 85% to the binary point Mg 0, Sb 5, Ag 95%. (c) The relationship on the line joining the binary point Mg 12.2, Sb 0, Ag 87.8% to the binary point Mg 0, Sb 6.4, Ag 93.6%.

from which it may be seen that the lattice-spacing relationship in the silver-rich ternary solid solution may be represented as a planar relationship between the linear relationships of the binary end members of the series.

### 5. GENERAL DISCUSSION

It is interesting to compare the lattice-spacing relationships in the aluminium-rich and silver-rich ternary solid solutions which have so far been investigated.

#### (a) *Aluminium-Magnesium-Copper*

In the aluminium-magnesium-copper system, there is a fair degree of solid solubility, the ternary solid solution coming into equilibrium with the ternary compound  $\text{Al}_2\text{MgCu}$ , which is not generally regarded as a compound of the normal valence ionic type. The aluminium lattice is expanded by magnesium but contracted by copper in solid solution, and in the ternary system the resultant effect of the two solutes appears to be almost strictly additive, with, however, the slightest suspicion of a contraction. The additive effect in this ternary solid solution is not unexpected, in view of the absence of marked ionic attraction between copper and magnesium.

#### (b) *Aluminium-Magnesium-Silicon*

In this system, the marked ionic interaction between magnesium and silicon is reflected in a greatly restricted ternary solid solution, which comes into equilibrium with the binary compound  $\text{Mg}_2\text{Si}$ . This may be regarded as a normal valence compound of the ionic type. The lattice-spacing relationships for the binary end members of this system are similar to those in the aluminium-magnesium-copper system. Magnesium expands, whilst silicon contracts, the aluminium lattice. However, in contrast to the aluminium-magnesium-copper system, the ternary aluminium-magnesium-silicon solid solution shows an unambiguous negative deviation of lattice spacing. This negative deviation is greatest along the quasi-binary line joining aluminium to the compound  $\text{Mg}_2\text{Si}$ , and moreover its magnitude increases linearly with the alloy content of the solid solution. Thus, the pronounced electrochemical difference between magnesium and silicon appears to produce a marked attraction between these two elements when they are both present in dilute solid solution in aluminium. Since the magnesium atom is larger than that of aluminium, whilst the silicon atom is smaller, it seems possible that two atoms of magnesium and one of silicon might come together as a cluster within the aluminium lattice without producing undue local distortion of the lattice. Thus, the combined effects of electrochemical attraction and favourable geometry may allow the formation of  $\text{Mg}_2\text{Si}$  clusters within the solid solution.

#### (c) *Silver-Magnesium-Antimony*

The situation differs somewhat in the silver-rich alloys of the silver-magnesium-antimony system. If we take the heats of formation (or melting points) of the inter-

metallic compounds as a measure of their stability, it appears that the electrochemical effect is much more pronounced in the binary magnesium-antimony system than in the binary magnesium-silicon system. However, a consideration of the silver-rich ternary solid solution containing magnesium and antimony suggests that the strong electrochemical effect between magnesium and antimony is considerably reduced by dilution with silver. Thus the silver-rich silver-magnesium-antimony solid solution is much more extensive than the ternary aluminium solid solutions and, moreover, comes into equilibrium with an electron compound and also with a ternary compound in addition to the binary compound  $\text{Mg}_3\text{Sb}_2$ . It should also be noted that both magnesium and antimony atoms are larger than that of silver.

The experimental observations of the present work suggest a purely additive lattice-spacing effect when magnesium and antimony are dissolved in silver, and if the negative deviations found in the aluminium-magnesium-silicon system result from a combination of electrochemical attraction and favourable atomic sizes, this additive effect in the silver solid solution may be due to the lesser probability of three large magnesium and two large antimony atoms congregating together in the lattice of small silver atoms, the silver lattice being in any case more rigid than that of aluminium.

It is possible that, in addition to the size considerations outlined above, the dilution of  $\text{Mg}_3\text{Sb}_2$  with silver attenuates the electrochemical attraction much more effectively than does the dilution of  $\text{Mg}_2\text{Si}$  with aluminium. Some evidence for this is given by the form of the respective solid-solubility limits.

### ACKNOWLEDGEMENTS

The authors' thanks are due to Professor F. C. Thompson for research facilities and to the Ministry of Supply and the Royal Society for financial assistance.

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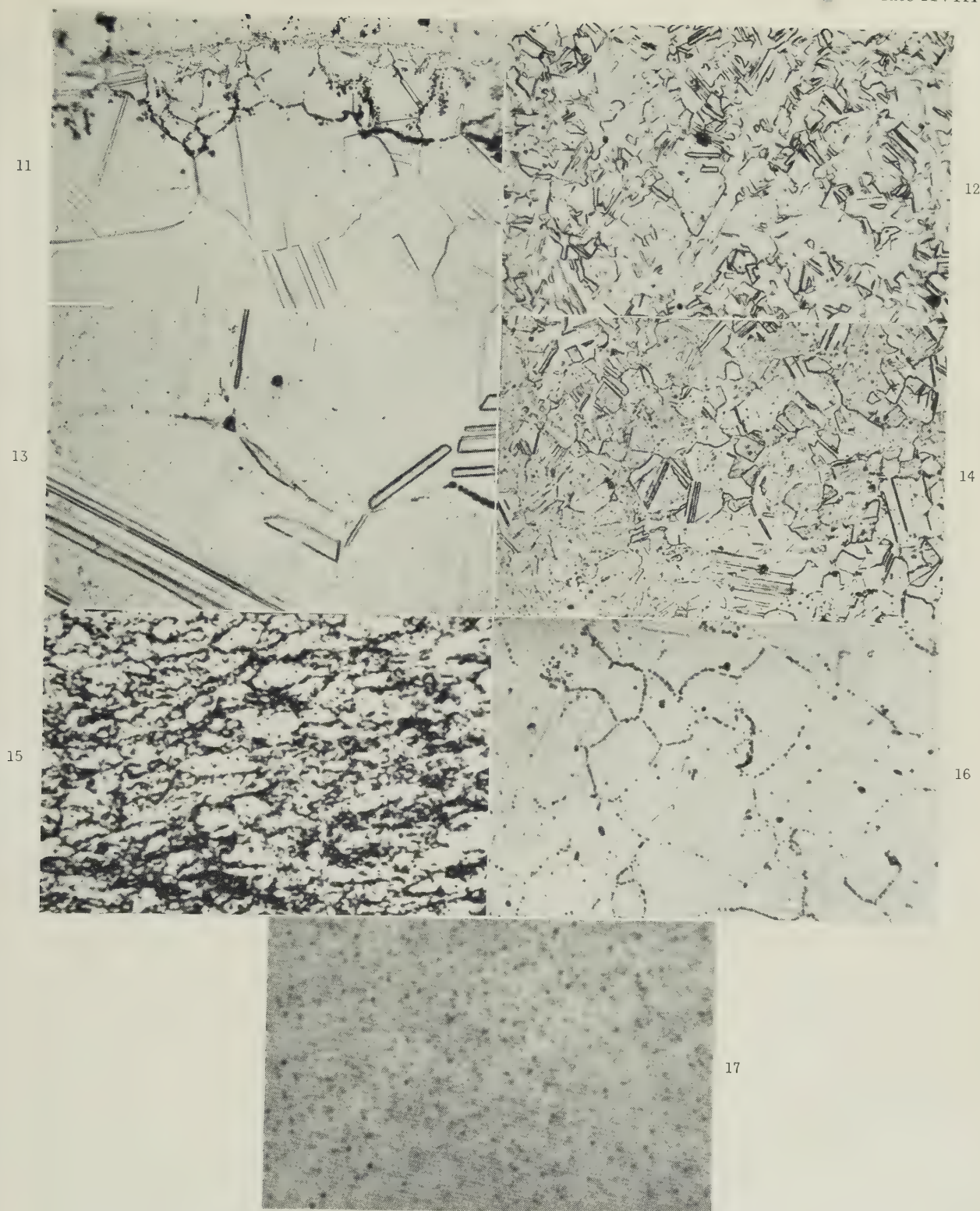


FIG. 11.—Oxidation Occurring in the Grain Boundaries near the Surface of a Silver-0.25% Aluminium Alloy Annealed in a Silica Tube.  $\times 100$ .

FIG. 12.—Silver-0.13% Silicon Alloy Vacuum-Annealed at  $675^{\circ}\text{C}$ . for 20 hr.  $\times 125$ .

FIG. 13.—Silver-0.13% Silicon Alloy Vacuum-Annealed at  $920^{\circ}\text{C}$ . for 20 hr.  $\times 125$ .

FIG. 14.—Silver-0.13% Silicon Alloy Oxidized at  $650^{\circ}\text{C}$ . in Oxygen for 20 hr. and then Reheated in Air at  $920^{\circ}\text{C}$ . for 20 hr.  $\times 125$ .

FIG. 15.—Silver-0.25% Aluminium Alloy Oxidized at  $850^{\circ}\text{C}$ ., Cold Rolled, and Heated in Oxygen at  $800^{\circ}\text{C}$ . for 20 hr. and at  $930^{\circ}\text{C}$ . for 20 hr.  $\times 1000$ .

FIG. 16.—Silver-0.13% Silicon Alloy Oxidized at  $650^{\circ}\text{C}$ . and Vacuum-Annealed at  $850^{\circ}\text{C}$ . for 20 hr.  $\times 1000$ .

FIG. 17.—Silver-0.25% Aluminium Alloy Oxidized at  $650^{\circ}\text{C}$ . Electropolished.  $\times 2000$ .

## PHOTOMICROGRAPHS OF COPPER-MANGANESE-ALUMINIUM ALLOYS.

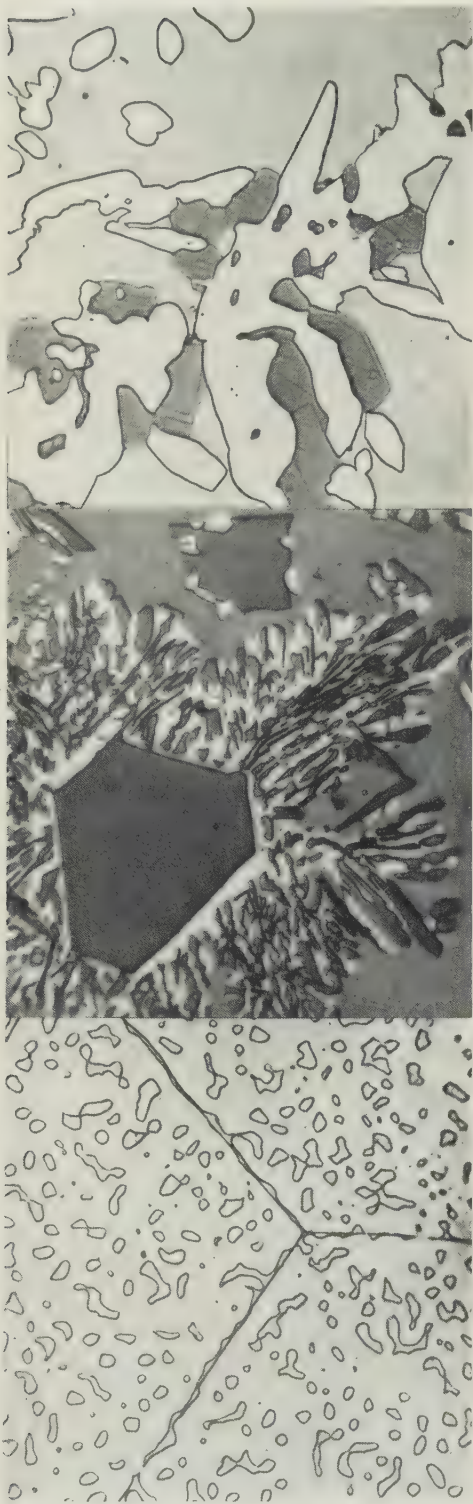


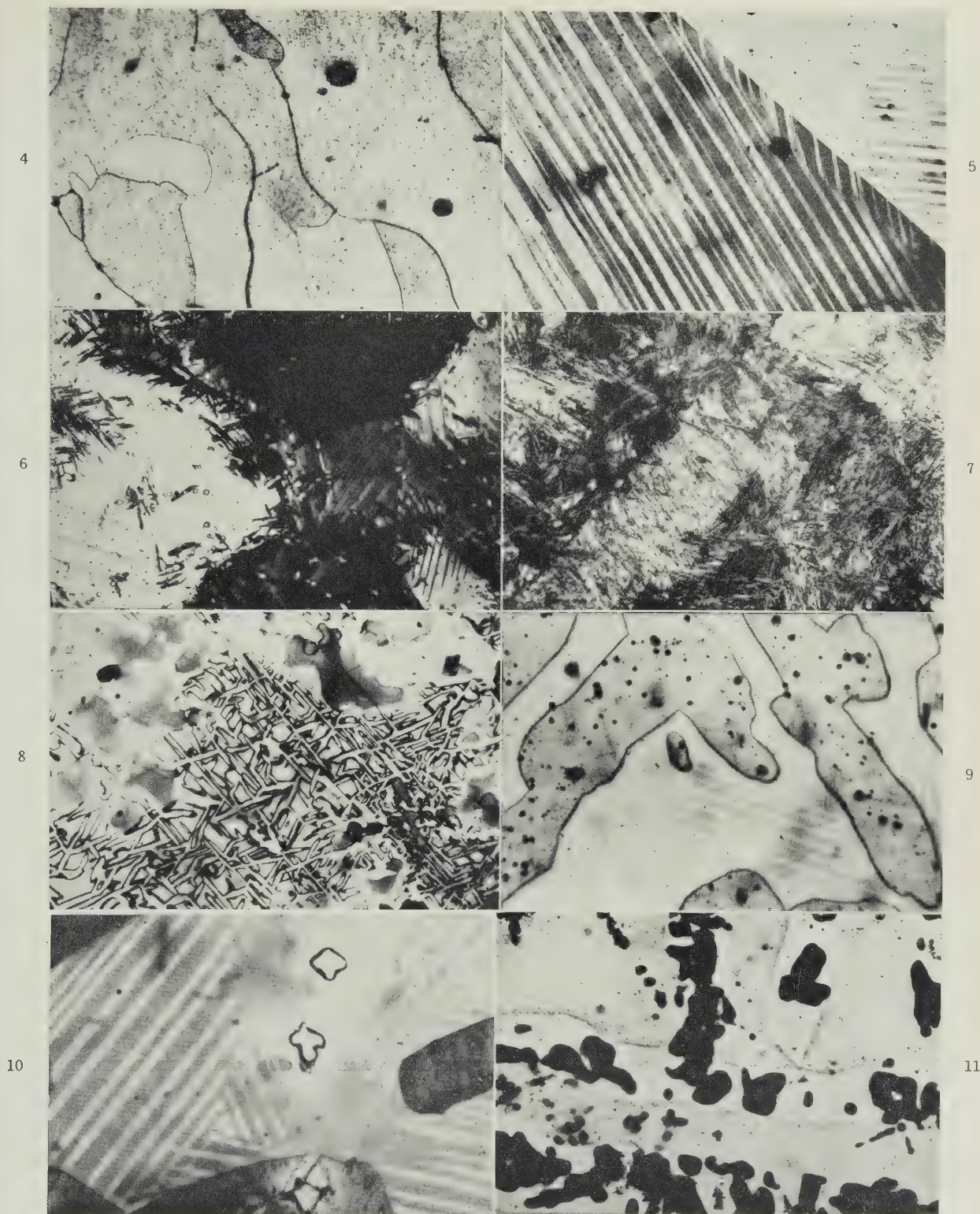
FIG. 11.—Alloy Containing Approximately 20 wt.-% Manganese and 8 wt.-% Aluminium. Annealed at 525° C.  $\alpha$  (light) +  $\beta$  (half-tone) +  $\text{Cu}_3\text{Mn}_2\text{Al}$  (dark).  $\times 600$ .

FIG. 12.—Alloy Containing Approximately 15.5 wt.-% Manganese and 11 wt.-% Aluminium. Annealed at 400° C.  $\beta$  (half-tone) +  $\gamma$  (light) +  $\text{Cu}_3\text{Mn}_2\text{Al}$  (dark). Eutectoid of ( $\gamma$  +  $\text{Cu}_3\text{Mn}_2\text{Al}$ ) growing from a large  $\text{Cu}_3\text{Mn}_2\text{Al}$  particle into  $\beta$ .  $\times 800$ .

FIG. 13.—Alloy Containing 5.8 wt.-% Manganese and 11.6 wt.-% Aluminium. Annealed at 500° C.  $\beta$  (outlined) +  $\beta_1$ .  $\times 400$ .

Etched in aqueous chromic acid solution.



MICROSTRUCTURES OF MANGANESE AND MANGANESE ALLOYS.  $\times 250$ .FIG. 4.— $\alpha$ -Manganese. Heated for 5 weeks at 650° C. in argon.FIG. 5.— $\gamma$ -Manganese. Water-quenched from 1100° C.  $\gamma$  phase.

FIGS. 6-10.—Manganese-3.1% Nickel Alloy. Water-quenched from 1100° C., and reheated to:

FIG. 6.—250° C.  $\alpha + \gamma$ .FIG. 7.—400° C.  $\alpha + \gamma$ .

FIG. 8.—500° C. 3-phase.

FIG. 9.—600° C.  $\alpha + \gamma$ .FIG. 10.—800° C.  $\beta + \gamma$ .

FIG. 11.—Manganese-5.2% Nickel Alloy. Water-quenched from 1180° C. and reheated to 700° C. 3-phase.





## SOME METALLURGICAL ADVANCES: HOW AND WHY THEY OCCURRED\*

By PROFESSOR DR. WERNER KÖSTER,\*\* MEMBER

### SYNOPSIS

The lecturer describes a number of important advances in the field of metallurgy (age-hardening alloys, stainless steels, permanent-magnet alloys, &c.) in order to demonstrate the numerous and varied ways in which discoveries may come about. In conclusion, he considers briefly the future of metallurgy as an independent science.

### I.—INTRODUCTION

We live in an age when research and science play a larger part than ever before in the lives of all peoples, and yet hardly anybody stops to think how inventions and discoveries come about. It is taken almost for granted that one technical advance will follow another, and that new ideas will replace existing ones.

Scientists and research workers carry on their work almost anonymously, and even other investigators in their own particular field rarely have any idea what steps have led them to the results they produce. Nevertheless, in this profession, as in others, it is the human element that counts. I personally confess that I can become really enthusiastic about a paper only if I know the author and can even imagine the intonation with which he himself would read it. This is one of the main reasons why I consider it so important that people working in the same field should meet one another, and it is from this point of view that I especially welcome this year's joint meeting of the Institute of Metals and the Deutsche Gesellschaft für Metallkunde.

In my opinion it is fascinating to trace the devious paths a research worker may have followed before he arrived at his final knowledge and discoveries. Sometimes it may be a question of the gradual perfecting of experimental apparatus or the systematic pursuit of an idea; on other occasions success may arise from deliberate search for the solution to a problem only he believes possible at all, or the recognition of the importance of some apparently insignificant factor; it may even be the appreciation of a phenomenon already known but completely neglected; or again success may come simply by a sudden inspiration, or as the outcome of a long, patient, and plodding series of experiments.

### II.—IMPORTANT DISCOVERIES

I should like to tell you, quite briefly, the story of some advances in our special field of metallurgy, laying particular emphasis on the extent to which scientific work depends on the personality of the scientist himself

and also on the time in which he lives, and I should like to show how these and other influences interact to produce the final achievement: scientific and technical success.

#### 1. DURALUMIN

I shall begin with the discovery of "Duralumin", which took place 50 years ago, almost to the day, in the Zentralstelle für wissenschaftliche technische Untersuchungen, directed by R. Sriebeck, at Neubabelsberg, near Berlin. Alfred Wilm<sup>1</sup> had just carried out some hardness tests on an aluminium alloy containing copper, manganese, and magnesium—in other words, Duralumin—after quenching from 520° C. It was a Saturday in September 1906, and so work was not resumed until the following Monday. A check test then showed that the hardness was much higher than it had been on Saturday. This naturally surprised Dr. Wilm. He carefully investigated the changes in mechanical properties of the alloy in relation to ageing time, and in this way came to recognize the phenomenon of age-hardening which has since become so important in metallurgy. Legend has coloured the story and has it that Wilm—an enthusiastic yachtsman—spent a long week-end on the lakes around Berlin, not returning to work until late on Monday. As you, Ladies and Gentlemen, hail from the country where the week-end was invented, you may prefer to believe this version, which ascribes the success to Wilm's adoption of that pleasant way of life. It was another fourteen years before Merica, Waltenberg, and Scott<sup>2</sup> recognized the constitutional conditions necessary for the ageing of alloys to take place, and explained the changes in properties which up till then had been considered anomalous. Whichever story we accept, the discovery of Duralumin was due to a purely chance observation, which, without any knowledge of the internal changes in the alloy, led to the correct conditions of heat-treatment.

#### 2. STAINLESS STEEL

Only a few years later, another very important alloy was discovered, but in this case the story is quite different, for the results were achieved by careful metallurgical and corrosion investigations. The new material

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was the austenitic stainless steel containing 18% chromium and 8% nickel, known in Germany as V2A. It was produced in December 1910 at the Krupp works at the instigation of B. Strauss, during a search for a heat-resistant material. In composition it was not new, since steel of that type had been made for other purposes by L. Guillet in 1906 and W. Giesen in 1909. On account of the comparatively high carbon content, which was in accordance with metallurgical practice in those days, it proved practically impossible to work the steel. Two years later, in September 1912, Maurer<sup>3</sup> noticed the high corrosion-resistance of this chromium-nickel steel, simply because it had not become rusty in the laboratory atmosphere. That fact induced him to experiment with its heat-treatment. While completing his doctor's thesis under Osmond, he had gained some experience in the field which led to his success in quenching the steel in the austenitic state from 1150° C. Already in October 1912 it was possible to apply for a patent for the commercial use of the corrosion-resistant austenitic chromium steel. Stainless steel is, therefore, the outcome of the work of a metallurgist whose scientific knowledge of the heat-treatment of steel was ahead of his time, and who, in addition, made use of the work of W. Borchers and P. Monnartz on the electrochemical behaviour of iron-chromium alloys.

There is, however, a similarity between the two stories of Duralumin and stainless steel; in both cases it was not a given problem that had to be solved, but the successful exploitation of a chance observation. It is just the fact that the phenomena were noticed and recognized as being important that lends to these two stories the pioneering touch. This opens up the question of the causes which may lead to a fundamentally new solution to a problem. Is it possible to find such a solution intentionally, as, for instance, to answer a specific question, or in what other way can it be done? Instead of talking about this in general terms, I would like to show, by a few individual examples, what really happens. I hope you will forgive me if I bring some of my personal experiences into the next story, which concerns age-hardenable permanent-magnet alloys.

### 3. PERMANENT-MAGNET ALLOYS

If, when I entered the research department of the Vereinigte Stahlwerke A.G. in 1927, I had been given the task of developing permanent-magnet alloys of higher coercivity than the existing ones, looking back now, I should probably have suggested the analytical approach, that is to say, the broadening of existing knowledge, but not the introduction of anything fundamentally new. I should have tried to feel my way gradually to the highest possible value attainable within the limits of the current technique. At the time, hardened carbon steel alloyed with cobalt was the best material for the purpose. This could no doubt have been improved by alterations in the carbon content and the alloying conditions, and the selection of the optimum alloy composition by a gradual process of elimination. That procedure is widely used everywhere to improve products, but it is generally a very tedious job. It can certainly be very successful, as has been proved, for instance, in the reduction of the power loss in transformer sheets: that was 2 W./kg. when silicon

iron was first introduced, and is now only  $\frac{1}{2}$  W./kg. Such a procedure forms the basis of all research work that consists in carrying out a large number of tests, but it rarely leads to a fundamentally new approach to a problem, always assuming, of course, that a new solution is possible.

I may be able to make this a little clearer by an example from geography. If we take the known data as a valley enclosed by mountain ranges, a process of gradual elimination will certainly serve to reveal the most fertile soil in the valley. It will not, however, help us to discover whether there are any neighbouring valleys offering far better conditions. For that purpose, expeditions into the unexplored territory will be necessary, and we shall have to leave our valley and cross the mountains. That expedition will have to be made at random, with no compass to guide us, but it may lead to an unknown valley with unexpected riches. Quite often there may be, to continue the analogy, additional mountains of preconceived ideas or prejudices to be crossed also.

The latest high-coercivity permanent magnets are produced from carbon-free iron alloys. The heat-treatment is completely different from the old hardening processes, and as a result, the alloys contain very finely dispersed particles of a second crystal structure. Still looking at the matter from our vantage point of present-day knowledge, it appears that this result could doubtless have been achieved on the basis of the theory of the effects of alloy structure on magnetic properties. Today, extensive data are available on the effects of finely dispersed particles of a second phase on the mechanism of magnetization. On the basis of that information, the composition of permanent-magnetic alloys might have been deduced in the same manner as new materials for the telecommunications industry have been developed from a theoretical knowledge of the effects of mechanical stresses. Such theoretical knowledge was, however, not available at the time of which I am speaking, and in actual fact it was the practical findings that formed the starting point for the development of the theory.

Leaving all this "what might have been" aside, I will tell you what actually happened. During my first job as a metallurgist, with Schweizerische Metallwerke Selve und Co., Thun, I had noticed that tensile tests on a certain type of brass sometimes showed a slight kink in the stress/strain diagram at the yield point.<sup>4</sup> This feature is unusual in non-ferrous metals and curiously enough nobody had up till then paid any attention to it. I investigated the matter and arrived at the conclusion that a certain structural arrangement was responsible. When I later joined the Research Department of the Vereinigte Stahlwerke A.G., whose director gave me a free hand in the choice of my research subject, I thought I would follow up this question in relation to iron. A very marked plastic-flow range at the yield point of iron, which is characteristic of the stress/strain curve, might well be attributable to the structure too. I started with the assumption that finely divided iron-carbide particles at the grain boundaries were responsible for the phenomenon. From that I deduced that the solubility of carbon in  $\alpha$ -iron increased with rising temperature, though only very little—about 0.02%. That is the constitutional precondition for the age-hardening processes which I mentioned above, but it was unknown in iron at the time. I extended my study



on the hardening of iron from the mechanical properties to the magnetic characteristics. In the course of this work, I noticed a slight increase in coercivity, which is the measure of quality of a permanent magnet.<sup>5</sup> This increase appears if the previously dissolved iron carbide deposits again in fine dispersed form on slight reheating of the sample. The coercivity increased from 2 to 5 Oersteds. The poorest magnet steel has a coercivity of 60 Oersteds. I had not yet got a permanent magnet, therefore, but I had a starting point from which to develop one; a new range of facts had come to light as a result of the investigations of a matter as far removed from magnetism as the kink in the stress/strain curve.

The approach for finding the material with the desired technical qualities was now obvious. Once the objective is fixed, it is easy to plan research. It was necessary to investigate systematically all iron alloys that might be expected, from their constitutional diagrams, to possess ageing properties. Working my way through the binary to the ternary alloys, I soon produced an iron-cobalt-molybdenum alloy having a coercivity of 350 Oersteds.<sup>6</sup> The highest-quality hardened cobalt steel at the time had a coercivity of 250 Oersteds, and had, therefore, been surpassed. The best magnet alloys now chiefly used in industry are, however, not my product, but are due to a Japanese research worker, T. Mishima.<sup>7</sup> He himself has told me the story of his endeavours to improve the iron-nickel Invar alloy by the method of progressive elimination. By adding aluminium, however, he entered another field of facts and so by chance provided the basis of the still unexcelled Alnico magnet alloys.

Now why was this particular success not achieved by research based on a knowledge of the interrelationship of the structure and properties? The answer is that thirty years ago we did not know the constitution of all the binary and ternary iron alloy systems. Had this knowledge been available, it would have been very easy to select the most suitable alloys by testing their magnetic properties, but as it was, I had to work out the systems myself; and when I got to the ternary systems I had to rely on conclusions drawn from the constituent binary systems, and so passed over the iron-nickel-aluminium alloys, in which the constitutional conditions required for age-hardening develop in the ternary alloys only.

This shows the value of data-collecting research, the hard work of assembling facts. It may seem very one-sided, especially if it is carried on continuously in an Institute, and it may become somewhat like routine drudgery, but the day comes when the information so amassed will be needed, and if it is not available, will be sorely missed. The story of the hardenable magnet alloys illustrates the true value of this aspect of research to industry and technical progress. The pure scientist may be content to have found a new principle, but the technologist must endeavour to produce the best possible practical result in the interests of progress. Accordingly, it is always advisable, when a new process or method of selection becomes available, to put as many trained personnel as possible on to the job of obtaining all additional information pertaining to the subject in question.

Pure science, however, also needs collections of data. Utilization of numerical data leads to the understanding of relationships on a wider basis and the establishment of

mathematical formulæ and thence to a true understanding of the phenomena concerned.

Let us return once more to the hardenable magnet alloys. The highest coercivity values are today obtained with Alni alloys cooled in a magnetic field. The first experiments in this connection were carried out by your compatriots—Oliver and Shedden.<sup>8</sup> They found an improvement of about 20% in a certain alloy and, on the basis of the theory as it then stood, they felt that that was exactly the effect to be expected. They published their results and left the matter at that.

Jonas,<sup>9</sup> of N.V. Philips' Gloeilampenfabrieken, Eindhoven, was not deterred by the report of Oliver and Shedden—though it was at that time acclaimed by a number of prominent physicists—from seeking an alloy that would respond even further to treatment in the magnetic field. He was firmly convinced—practically to the point of obsession—that a systematic study of all iron-nickel-aluminium alloys must lead to success. In actual fact it did so, and to a surprising degree. The coercivity could be increased to three times its former value. It is very sad that Jonas should have had no reward for his invention, at least not in Germany, for—and now theory plays for the second time a twilight role—the German patent office refused a patent, mainly because of its inadequate theoretical conception of the treatment in a magnetic field. Yet of the three features required by patent law: novelty, value of discovery, and technical progress, the last, at least, was beyond doubt very great. With that we leave the story of hardenable magnetic alloys, which, I think you will agree, is certainly not lacking in surprising twists.

#### 4. S.A.P.

I would like to illustrate, by another example, how far the actual results achieved in research may be from the objective originally envisaged, and how impossible it is to order or force a discovery. In short, it is nearly always a question of the research worker being alert enough to recognize something new when it presents itself. There is the case of S.A.P., the sintered pure aluminium material, which has, amongst other properties, a high resistance to heat. Professor von Zeerleder<sup>10</sup> reports on its discovery as follows: If there had been a request for an unusually heat-resistant aluminium alloy, the outcome would, in all probability, have been unsuccessful, for it would have been impossible to find the solution to the problem by making a conventional approach in the light of existing knowledge. In actual fact, the research arose from a demand for the production by powder metallurgy of a pure standard alloy for spectrographic analysis. As the properties of the sintered bodies became known and the difficulties of production were overcome after some initial setbacks, the important S.A.P. material came into being.

I should like to answer here the question: Can research be influenced or guided? From what I have just said, you might easily feel that this would be a dubious undertaking. No doubt it would seem difficult to direct scientific research if the way that will lead to results is unknown, in addition to which, the aptitude of the research worker must not be overlooked. Well, the answer seems to be that if research is to be helped to yield the best returns, the simplest and most reliable method would be to aid science in general everywhere,

and to give successful scientists all possible assistance so that they can pursue their work without hindrance. That would result in the fullest utilization of the total scientific potential, and would lead to the highest possible standard of science. Science, that is to say the sum total of experience, may be compared to a reservoir that is fed by research, whilst the outflow runs into the various channels of industry. If this reservoir is to be a constant source of power, it must not be constantly tapped without steps being taken to maintain the level. The best way to accomplish that is by permitting freedom of research. Research should not be burdened with expectations and demands which are alien to its very character. No condition should be attached to the payment of money for research other than that it should be used for its proper purpose, and there should be no demand for a direct monetary return. Research is like a plant which will produce its fruit in the right place, at the right time. This is how it has been in the past, and, moreover, experience shows that the technical utilization of scientific discoveries is achieved more quickly now than ever before.

### 5. THE SIGNIFICANCE OF DISLOCATIONS

I would now like to tell you of a rather peculiar experience, which others probably share with me, and which concerns a matter of great importance in metal physics today. I mentioned a hypothesis which I had worked out to account for the presence of a kink in the stress/strain curve of brass at the yield point, but today we know that it did not prove correct. The kink is due not to a change in structure, but to a change of position of the foreign atoms present. The deductions I had made from the experiments were, therefore, not wrong logically. I associated the region of plastic flow not with its true cause, which was then completely unknown, but with an internal change which takes place simultaneously, though having no direct connection with it. Nevertheless, this wrong assumption, used in a consistent way, brought fruitful results. Today we know that the kink in the stress/strain diagram is caused by dislocations anchored by foreign atoms.

Many paths had to be explored before the full importance of the lattice imperfections we now know as dislocations in the atomic structure of solids, was appreciated. In an ideal lattice, let us say a simple cubic lattice, the atoms occupy the corners of a cube. In two-dimensional representation they appear as a square network of dots. Each row contains the same number of atoms, so that the atoms in two neighbouring rows are opposite to one another. Let us assume that there are nine atoms in each row, and that we introduce an additional atom into one row; then the pattern will no longer fit. A picture similar to the Vernier scale is created, with nine atoms facing ten in the next row over the same distance. This means that the rows are strained with respect to each other, the one being under compression, the other under tension. A local defect of this kind, introduced into a lattice plane of the crystal, is termed a dislocation.

The concept of lattice defects was originally introduced as a hypothesis to interpret certain experimental observations for which there was no other explanation. Prandtl<sup>11</sup> entitled an early essay on the subject: "An Imaginary Model for the Kinetic Theory of Solid

Bodies". In this the Vernier scale was first cited to explain structural defects in crystals. With the aid of this model, it was possible to make a mathematical approach to problems such as elastic hysteresis, elastic after-effect, and the dependence of strain on rate of flow. The work-hardening process, however, could not be interpreted by means of the model, which, incidentally, was mentioned as early as 1913 by von Kármán<sup>12</sup> in the "Enzyklopädie der mathematischen Wissenschaften". Prandtl himself did not find the time to report on his work until 1928.

Independently of this work, Dehlinger<sup>13</sup> approached the problem in 1929 by developing a simple model for the mathematical treatment of the cold-worked state. He introduced the idea of hooked lattice deformations which link together lattice regions of different orientation. This concept is very nearly valid in our present-day ideas regarding neighbouring pairs of dislocations of different signs. The breakdown of such hooks during recrystallization, as he described it, corresponds closely to the annihilation of dislocations of different signs.

In 1934 Polanyi<sup>14</sup> and Orowan<sup>15</sup> realized that lattice disturbances of the Vernier type could explain the observed process of plastic deformation by translation under stress. Translation means that portions of a metal move along certain crystal planes, the slip planes, in a definite crystallographic direction, the direction of slip. After deformation, a practically undistorted lattice once more exists. Slip in an ideal crystal lattice would therefore mean that one lattice region moves along the slip plane by the distance of one atom spacing. The force required to effect this in theory would have to be about 1000 times greater than in fact it is for real crystals. This contradiction is explained by introducing the concept of lattice defects. The paper by Polanyi in which, incidentally, the term dislocation was first used, was entitled "A Type of Lattice Distortion which Might Render a Crystal Plastic".

All the work just referred to was based on the concept of special models. It was left to Taylor,<sup>16</sup> in 1934, to initiate the systematic development of the dislocation theory, independently of any particular model, by combining the atomic concepts with the mechanics of deformable bodies. Between 1905 and 1907 Weingarten<sup>17</sup> and Volterra,<sup>18</sup> in Italy, had worked out a mathematical theory for the relation of internal stress to residual deformation. Taylor was acquainted with this work, as he himself was a mathematician. While working on plastic-deformation experiments, he had the inspiration of trying to apply Weingarten and Volterra's theory to dislocations. In 1934 he dealt with a slight imperfection of the lattice round a dislocation by means of elastic theory, in spite of the fact that the latter considers the crystal as a continuum and pays no attention to its atomic structure. With that step he had entered upon a very promising line of research, which was followed up by J. M. Burgers<sup>19</sup> in 1939, in an outstanding way.

In course of time the theoretical models became a reality. They no longer represented imaginary hypotheses, and it gradually proved possible to explain various phenomena quantitatively, and even to make predictions with their aid. They have, for instance, proved most valuable in the explanation of the plastic behaviour of metals and processes of polymorphic trans-



formation, and in the study of crystal growth, mosaic structure, and grain boundaries, to mention only a few subjects. In addition, a large number of experimental observations have been made which confirm the truth of the dislocation theory. Of these, I would mention the spiral growth of many crystals, and the proof afforded by etch pits.

A scientific hypothesis and an inspiration thus served to open up a wide field of phenomena to exact investigation. Begun in order to solve the puzzling contradictions between experiment and theory, the work has widened our conception of the statics and dynamics of atoms and solid bodies very considerably.

#### 6. DAMPING CAPACITY

A sound idea always leads to progress in research. Good ideas are invaluable because they provide the key to an understanding of known phenomena and make possible a methodical investigation of their causes. It had been known for decades that the time of acoustic resonance of a rod of commercial iron set in vibration is a minimum just above room temperature, the elastic vibrations being damped particularly strongly at that point. Snoek,<sup>20</sup> of N.V. Philips' Gloeilampenfabrieken, Eindhoven, proposed a mechanism by which dissolved carbon and nitrogen atoms enter the space lattice in the elastically extended direction, and then jump from one lattice site to another during vibration. This idea has proved very fruitful. Damping capacity is used nowadays for the quantitative determination of carbon and nitrogen dissolved in iron or other body-centred cubic metals, and minute quantities—as little as  $10^{-5}\%$ —can be determined. The method is also used to estimate the solubility curve of such admixtures, for measuring their coefficient of diffusion, for investigating the kinetics of segregation, for measuring the dislocation density, and for many other purposes.

#### 7. TURBINE-BLADE MATERIAL

In the course of our survey only one example is still missing, that illustrating the solution of a problem solely by the conscious application of scientific perception. Clearly one of our objectives is to develop materials with desired properties by systematic research rather than to depend on pure chance. In this connection I would refer to an alloy known as Nivco which is used in steam-turbine construction at temperatures up to about  $630^{\circ}\text{C}$ . Materials to satisfy the requirements of such an application must possess high strength and high mechanical damping at service temperatures and must also have high chemical resistance. The required mechanical damping can, according to the results of Coehardt's work<sup>21</sup> in the laboratories directed by C. Zener, be supplied by means of the magneto-mechanical damping effect investigated by Becker and Kornetzki<sup>22</sup> in 1936. From this it follows that one essential property of the alloy sought must be a high Curie temperature and high magnetostriction. The second requirement of high strength at elevated temperatures implies that it must be composed of face-centred cubic metals. These two requirements, and luckily also the third one of adequate chemical resistance, can be satisfied by cobalt-nickel-base alloys. Age-hardening and improvement of these alloys by the addition of small

amounts of other metals led finally, by well-founded preliminary consideration, so to speak on the drawing board, to an excellent alloy for turbine blades.

### III.—THE FUTURE OF METALLURGY

I have given you some specific examples of the sources of progress in metallurgy, and I should now like to trace the development of metallurgy as a whole. I think this is a matter of fundamental importance to your Institute and our Society, because it is from a consideration of the way in which metallurgy has developed that decisions must be made on the methods that we have to adopt to achieve our objectives, to arrange our meetings, to compile our publications, and to train the coming generation.

Metallurgy has established a field of its own by the co-operation of workers in various related sciences. The smelting and foundry industry, pure and physical chemistry, crystallography and engineering have all contributed to the creation of a field of science centred on metal, that is to say, on a material. The initiative came from the industry which produces, processes, and utilizes the metal. I would refer to men like Sorby, Roberts-Austen, and Rosenhain in your country, and Martens, Heyn, and Tammann in Germany. The backbone of metallurgy is a knowledge of the constitution and properties of metals and alloys and the changes brought about in them by thermal or mechanical treatment. This definition shows that science and industrial practices are closely interwoven, and it is also the justification for the existence of metallurgy as a separate field of science, since the subject is dealt with neither in physical nor chemical text-books. It also justifies the specialized teaching of the subject at universities and technical colleges.

During the first period of its development, metallurgy could properly be described as the science of metallic materials, for it was mainly concerned with the requirements of the metal industry. The extent of knowledge in that period, as far as Germany is concerned, is represented by the "*Lehrbuch der Metallkunde*", by Gustav Tammann, last published in 1932.

This first period, which may be called the centripetal one, because during its course a self-contained science of metallurgy was built up, was followed by a, so to speak, centrifugal one. The critical point in this development may be regarded as having occurred in the year of Gustav Tammann's death, 1938. Then physicists, chemists, and others took possession of various aspects of metallurgy, and made them branches of their own special fields. Metal physics, in particular, has developed tremendously; on the basis of present-day physical knowledge, this branch of science explains the behaviour of alloys in terms of their atomic structure. Anyone who now desires a sound understanding of the structure of metals must be fully conversant with the theory of X-ray diffraction and the band model of the electron theory. No one can hope to develop magnetic materials with any kind of success unless he first masters the theory of ferromagnetism. The thermochemistry of alloys has passed into the hands of physical chemists who interpret equilibrium diagrams on a thermodynamic basis. Corrosion research requires a specialized knowledge of electrochemistry, whilst the plastic

deformation of metals is split up between theoretical physics for the micro-behaviour and applied mechanics for the macro-characteristics.

In other words, without a sound and thorough knowledge of the experimental and theoretical disciplines of other branches of science, individual problems in metallurgy can no longer be tackled. That means specialization within the field of metallurgy and a change of emphasis in the direction of the classical sciences. This has led to a situation very clearly portrayed by Dr. W. Hume-Rothery in his Socratic dialogue between the "Older Metallurgist" and the "Young Scientist".

The question that naturally arises from this is whether metallurgy, as such, is in danger of disappearing. It is obviously impossible for a metallurgist with the conventional training to be an expert in all aspects of the subject. I think we should here look at the various branches of science related to metallurgy. Neither the physicist, the crystallographer, nor the electrochemist can claim to be a metallurgist, though their work in various aspects of metallurgy is of fundamental importance, and can by no means be over-estimated.

The purpose of metallurgy as such is, however, to extract from the related fields of science everything that bears on metals. The metallurgist should have, on the scientific side, a working knowledge of physics, chemistry, and the technology of metals, and, on the practical side, be capable of supervising the quality of the metal at each stage of processing from the casting operation to the finished product.

In order to achieve that, it is necessary to add to the initial core of knowledge which contains the description of the fundamental phenomena, concentric spheres into which the results of scientific research can be fitted in an appropriate way. The new, mainly theoretical, concepts must be interpreted to the metallurgist whose knowledge lies more on the technical side of his subject, and aspects of present-day physics and chemistry must be suitably explained. The theories of the metallic state based on modern physics will have to be linked up with the more traditional aspects of metallurgy. An endeavour to solve this problem of our day, has been made in Germany by G. Masing—a Platinum Medallist of the Institute of Metals—in his "Lehrbuch der Metallkunde", which is soon to appear in a second edition.

I believe that both our societies have recognized the changes that have taken place in metallurgy in our time and are coping in their respective ways with the problems these changes have presented. As before, we need practical men in industry. Brass was rolled hundreds of years ago before anyone ever thought of dislocations in crystals. Nevertheless, it was only with the knowledge of dislocations that certain phenomena connected with the yield point of the metal could be explained; similarly, the electron theory is necessary to an understanding of the changes in properties that take place during the heat-treatment of brass and which were until recently unaccounted for. Therefore the practical man should take note of any progress in sciences, the fundamentals of which he has learnt during his training. On the other hand, it seems reasonable to ask the theoretical scientist not to consider it beneath his dignity to keep in touch with metallurgical practice and to consider its requirements. The purpose of our societies is to maintain contact with both sides in an endeavour to preserve

the unity between industry and science where metals are concerned.

Ladies and Gentlemen, I have come to the end of my lecture. I did not intend to give a weighty analysis of the methods of research and the mental make-up of the scientist, and I shall be gratified if I have succeeded in entertaining you, and, by a few stories chosen at random, have given you some kind of idea how advances in metallurgy come about.

For the young metallurgist my observations may provide self-confidence and trust, if any be needed. Possibly one is touched by a feeling of insufficiency on reading a perfect publication. Everything seems to be foreseen, well thought out from the beginning, free from chance. But it must be remembered, that perfect art implies a skill in presentation which omits all preliminary considerations, all wrong ways and errors, which draws a curtain over the painful work of the day, which summarily omits what my master Gustav Tammann used to call "the artist's pilgrimage".

I have, today, afforded you a glance at our cards, and shown you lively reality. You have seen how tortuous the paths of research can be. They are full of surprises, leading ever anew to developments in unforeseen directions, to knowledge where the researcher has not sought it, to technical applications where he has not expected them. So we can understand that, occasionally, the feeling takes possession of him that he is the led, rather than the leader. Max Planck was, as he often affirmed, a "reluctant revolutionary". But one thing is common to all true research. Its results are won in the course of unceasing, stubborn wrestling with problems in the service of knowledge. Compelling necessity drives the research worker unceasingly onwards, to the neglect of all else; his heart is engaged as well as his head. For each deeper insight, each original discovery, arises not only from cool calculation but is also the outcome of creative force and imaginative perception.

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# THE EQUILIBRIUM DIAGRAM OF THE SYSTEM COPPER-GERMANIUM\*

1731

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## SYNOPSIS

The equilibrium diagram of the system copper-germanium has been determined accurately in the region 22–100 at.-% germanium. Special attention has been paid to the diagram in the region 22–30 at.-% germanium, and it is thought that the phase boundaries have been established to within  $\pm 0.1$  or  $\pm 0.2$  at.-%. The existence of the  $\eta$  phase claimed by Betterton is confirmed, and the general form of the diagram resembles that proposed from X-ray data by Schubert and Brandauer (*Z. Metallkunde*, 1952, **43**, 262), but the boundaries of the phase fields are displaced in the direction of lower germanium content. The equilibrium diagrams of the systems copper-germanium and copper-silicon are compared.

## I.—INTRODUCTION AND PREVIOUS WORK

THE work described in the present paper forms part of a systematic investigation of the constitution of the alloys of copper with zinc,<sup>1</sup> gallium,<sup>1-3</sup> germanium,<sup>1,4</sup> and arsenic.<sup>5</sup> The equilibrium diagram of the system copper-germanium is characterized by the formation of an  $\alpha$  solid solution of germanium in copper, the liquidus for which up to 12 at.-% germanium has been determined by Hume-Rothery, Mabbott, and Channel-Evans,<sup>1</sup> who also established the solidus and the approximate limits of the  $\alpha$  phase in the solid state. The  $\alpha$  solid solubility curve was later determined accurately by the microscopical work of Hume-Rothery, Raynor, Reynolds, and Packer<sup>4</sup> and by the X-ray work of Owen and Roberts<sup>6</sup> and Owen and Rowlands.<sup>7</sup> With increasing proportion of germanium, the  $\alpha$  phase is succeeded by the  $\zeta$  phase with a close-packed hexagonal structure; the solidus and solid-solubility curves for the  $\zeta$  phase have been established accurately,<sup>4</sup> whilst liquidus curves are given by Weibke,<sup>8</sup> Schwarz and Elstner,<sup>9</sup> and Maucher,<sup>10</sup> though the rates of cooling employed by them were too great to ensure the highest accuracy.

On the germanium-rich side of the diagram, recent work in connection with the semi-conducting properties of germanium has shown the solubility of copper in germanium to be very small.<sup>§</sup> This is in agreement with the conclusions of earlier workers whose thermal analyses showed that the liquidus fell from the freezing point of germanium to a eutectic point at 35–38 at.-% germanium and 640°–650° C., but the exact temperature and composition were uncertain when the present work was started.

That part of the equilibrium diagram in the region 25–40 at.-% germanium has been in dispute, and the suggested versions are shown in Fig. 1 (a)–(d), in which the symbols used to designate the phases have been made uniform. These diagrams were determined mainly by thermal analysis at rates of heating or cooling too rapid for the attainment of true equilibrium conditions, and

some of them do not satisfy the requirements of the Phase Rule. There is general agreement that the  $\zeta$  phase is succeeded by a phase in the region of 25 at.-% germanium which undergoes a transformation at about 550° C. According to Schwarz and Elstner<sup>9</sup> and Maucher,<sup>10</sup> the high-temperature modification of this phase is formed peritectically at about 740° C., whereas Weibke<sup>8</sup> obtains a maximum on the liquidus at 749° C., but does not explain this and apparently still regards the arrests at 740° C. as being due to a peritectic reaction. In the Inorganic Chemistry Laboratory at Oxford, Betterton,<sup>12</sup> using microscopical methods, deduced the existence of a new phase, here denoted  $\eta$ , of slightly higher germanium content than the  $\epsilon_1$  phase; this has been confirmed in the present experiments, and accounts for some of the unexplained thermal arrests in the earlier German work.

Schubert and Brandauer,<sup>13</sup> in work published while the research now described was in progress, used high-temperature X-ray methods, and confirmed that the  $\zeta$  phase has a normal close-packed hexagonal structure. They concluded that the  $\epsilon$  phase is an orthorhombically distorted modification of the close-packed hexagonal structure, and the  $\epsilon_1$  phase a trigonally distorted form of the body-centred cubic structure. They describe the  $\eta$  phase as possessing a body-centred cubic structure containing lattice defects, the evidence for these being the existence of an extra line in the diffraction pattern. Schubert and Brandauer state that their results can be reconciled with those of Betterton, and appear to have altered some of their points to agree with the form of the diagram suggested by the latter author.

## II.—EXPERIMENTAL

### 1. METHODS

#### (a) Metals Used

The copper was of 99.998% purity, kindly presented by the British Non-Ferrous Metals Research Association.

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‡ George Kelley Reader in Metallurgy in the University of Oxford.

§ Thus, Hodgkinson<sup>11</sup> claims that the maximum solubility is 1 atom of copper in  $10^7$  atoms of germanium.

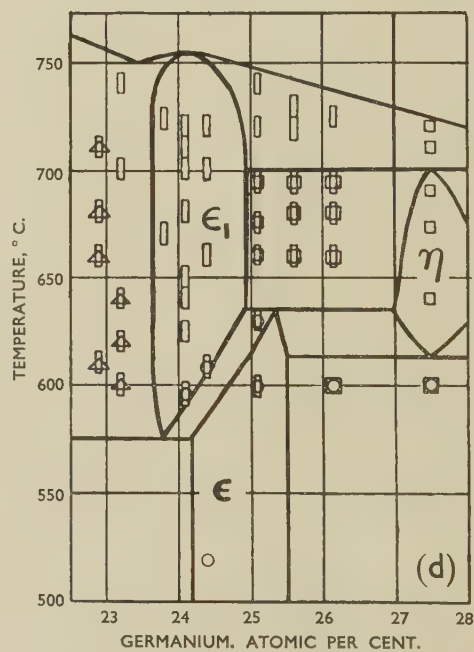
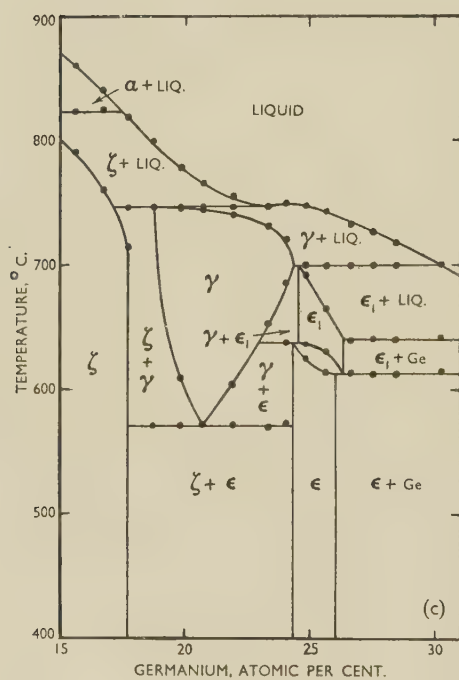
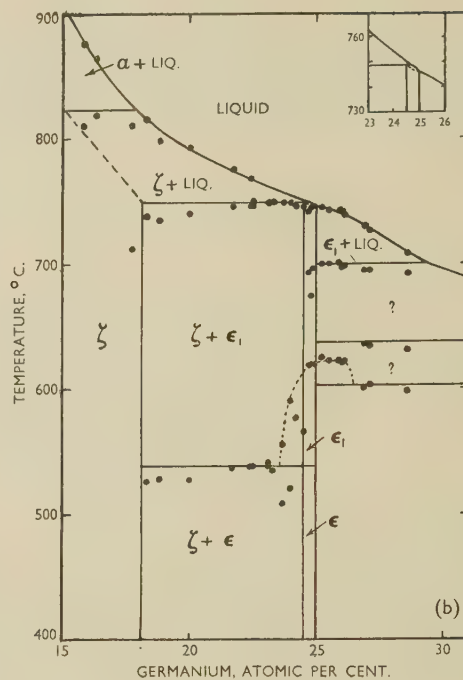
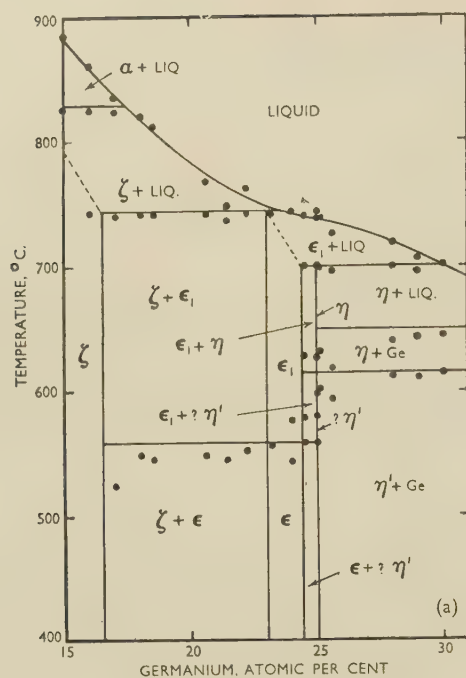


FIG. 1.—The Equilibrium Diagram of the System Copper-Germanium from 15 to 30 at.-% Germanium, according to (a) Schwarz and Elstner<sup>9</sup>; (b) Maucher<sup>10</sup>; (c) Weibke<sup>8</sup>; (d) Schubert and Brandauer.<sup>13</sup>



The germanium, supplied by Messrs. Johnson, Matthey and Co., Ltd., contained less than 5 p.p.m. of total impurities.

### (b) Thermal Analysis

For the cooling curves, the metals were melted in amounts of the order of 30 g. in tall narrow alumina crucibles provided with graphite lids. The crucible was placed in a cylinder of graphite, closed at one end, which surrounded the crucible entirely except at the base. A silica tube was inserted through a small hole in the closed end of the graphite tube, and a slow current of nitrogen passed between the graphite tube and the crucible, the entire assembly being inside a closed silica tube which fitted into a Nichrome-wound resistance furnace. A few chips of charcoal were placed on the melt, and experiment showed that, even when the nitrogen supply was stopped, oxidation was completely prevented. The melt was stirred continuously during the taking of a cooling curve, the rate of cooling at the liquidus point being of the order of 1° C./min. An accurate deflection potentiometer was used, and all the precautions described by (P. W.) Reynolds and Hume-Rothery<sup>14</sup> were taken; these included the checking of the potentiometer current and galvanometer sensitivity at the arrest point, and a test for thermal gradients in the ingot. The liquidus arrests were clear and well defined on the cooling curves and could be located to within 0.1–0.2° C. So far as the pyrometry is concerned, it is thought that the arrest points were established to an accuracy of  $\pm 0.5^\circ$  C., or better.

Twenty-two cooling-curve ingots were analysed for both metals, and the compositions by analysis proved to be in such good agreement with those calculated from the weights of metal used that it was thought justifiable to use synthetic compositions for some additional points. For certain of the germanium-rich alloys, economy of material was obtained by taking one cooling curve, and then remelting the ingot with a weighed amount of copper; this procedure had been found satisfactory with copper-gallium alloys,<sup>3</sup> and the final ingot was always analysed. All the chemical analyses were carried out by Messrs. Johnson, Matthey and Co., Ltd.

For the heating curves, a preliminary annealing treatment (near to the first expected arrest) was always given, and in most cases it was found that the temperatures of the peritectic and solid-state horizontals were established with greater certainty by heating than by cooling curves. The results of thermal analysis are given in Table I.

### (c) Annealing Technique

The alloys for microscopical work were prepared by melting under Analar potassium chloride in graphite crucibles, and were cast into heavy copper moulds in order to produce rods of  $\frac{3}{16}$  in. dia. with a very fine microstructure. They were usually given a preliminary annealing treatment at an appropriate temperature to establish a more uniform composition, followed by a final treatment at the required temperature. The annealing was carried out in sealed evacuated tubes of silica or hard glass, and the temperature was automatically controlled to within  $\pm 2^\circ$  C. of the desired value, whilst in some cases an accuracy of  $\pm 1^\circ$  C. was obtained. At the

TABLE I.—Results of Thermal Analysis.

Germanium, at.-% *	Arrests, ° C.		Corresponding Phase Change
	Cooling	Heating	
12.40	938	824	Liquidus $\alpha + \text{liq.} \rightarrow \zeta$
15.19	887.5	824	Liquidus $\alpha + \text{liq.} \rightarrow \zeta$
17.02	837.5	822.5	Liquidus $\alpha + \text{liq.} \rightarrow \zeta$
17.94	819.5		Liquidus
†18.88	804 743.5	743.5	Liquidus $\zeta + \epsilon_1$ eutectic horizontal
20.18	777.5 743.5 [539]	743.5 [564]	Liquidus $\zeta + \epsilon_1$ eutectic horizontal $\epsilon_1 \rightarrow \epsilon + \zeta$
21.67	752 743.5 [543]	743.5 [562]	Liquidus $\zeta + \epsilon_1$ eutectic horizontal $\epsilon_1 \rightarrow \epsilon + \zeta$
22.20	745.5 743 [544.5]	[561]	Liquidus $\zeta + \epsilon_1$ eutectic horizontal $\epsilon_1 \rightarrow \epsilon + \zeta$
22.97	745	[743.5]	Liquidus $\zeta + \epsilon_1$ eutectic horizontal
23.43	746.5 [558.5]	[560]	Liquidus $\epsilon_1 \rightarrow \epsilon + \zeta$
†24.01	745.5 [626] [546]	[696.5] 635 [558.5]	Liquidus $\epsilon_1 + \text{liq.} \rightarrow \eta$ $\epsilon_1 + \eta \rightarrow \epsilon$ $\epsilon_1 \rightarrow \epsilon + \zeta$
24.42	744.5 697 [629.5]	697 633.5	Liquidus $\epsilon_1 + \text{liq.} \rightarrow \eta$ $\epsilon_1 + \eta \rightarrow \epsilon$
25.45	741 698 629.5 608.5	698 636 614.5	Liquidus $\epsilon_1 + \text{liq.} \rightarrow \eta$ $\epsilon_1 + \eta \rightarrow \epsilon$ $\eta \rightarrow \epsilon + \text{Ge}$
26.13	736.5 697 608.5	698.5 614.5	Liquidus $\epsilon_1 + \text{liq.} \rightarrow \eta$ $\eta \rightarrow \epsilon + \text{Ge}$
27.35	729 697 640.5 610.5	698 642.5 614	Liquidus $\epsilon_1 + \text{liq.} \rightarrow \eta$ $\eta + \text{Ge}$ eutectic horizontal $\eta \rightarrow \epsilon + \text{Ge}$
28.95	714.5 696.5 641 611.5	699 642.5 614	Liquidus $\epsilon_1 + \text{liq.} \rightarrow \eta$ $\eta + \text{Ge}$ eutectic horizontal $\eta \rightarrow \epsilon + \text{Ge}$
30.53	694		Liquidus
32.0	685.5 641.5 611	642.5 613.5	Liquidus $\eta + \text{Ge}$ eutectic horizontal $\eta \rightarrow \epsilon + \text{Ge}$
35.39	662.5 642	642.5 614.5	Liquidus $\eta + \text{Ge}$ eutectic horizontal $\eta \rightarrow \epsilon + \text{Ge}$
36.26	649 642		Liquidus $\eta + \text{Ge}$ eutectic horizontal
37.82	646.5 642		Liquidus $\eta + \text{Ge}$ eutectic horizontal
40.74 46.02 †50.72 58.26 67.40 83.32 Pure Ge	674.5 709 736.5 775 816.5 881 937.5		} Liquidus

\* The compositions of the alloys are those determined by analysis except for the values marked †.

end of the treatment the specimen was quenched in a slush of ice and water.\*

#### (d) Microscopical Examination

The alloys were ground and polished by standard methods and, for etching, the most satisfactory reagent was found to be a mixture of equal proportions of 20-vol. hydrogen peroxide, and 0.880 aqueous ammonia. The microstructures were often rendered more complex by decomposition during quenching; these effects are described below.

#### (e) Chemical Analysis

The majority of the critical alloys which establish the boundaries of the phase fields were analysed. In many cases both copper and germanium were determined, and as there was no evidence of contamination, other alloys were analysed for copper only, and the germanium taken by difference. The compositions determined by analysis usually agreed to within 0.1 or 0.2% with those calculated from the weights of the metals used, the general tendency being for a very slight loss of germanium to occur. In the diagrams, the full points indicate that analysis was carried out on the actual specimen examined microscopically after annealing at the temperature concerned. The open points indicate either that another portion of the same ingot was analysed, or that synthetic compositions were employed reduced by 0.1% to allow for the general slight loss of germanium. It is thought that the open points are accurate to within  $\pm 0.3\%$ .

#### (f) Annealing Treatments

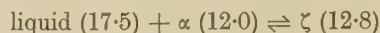
Ingot were usually first homogenized at a high temperature. For alloys which were subsequently to be annealed in the ( $\epsilon + \eta$ ), ( $\epsilon + \epsilon_1$ ), and ( $\epsilon + \text{Ge}$ ) phase fields, however, it was found better to proceed straight to the temperature of the final anneal, since very coarse structures were produced by high-temperature treatment if this took the alloy into the ( $\epsilon_1 + \eta$ ) two-phase state. The times of the annealing treatments were of the order of 1, 2, 3, 11, and 14 weeks at 700°, 600°, 550°, 450°, and 300° C., respectively. For many of the critical alloys, the anneals were repeated for double these times, and some of the 300° C. anneals were extended to 6 months, but no change in structure resulted from the longer treatment. Above 700° C. a few days' treatment was sufficient to produce equilibrium. For the solidus determinations, the previously homogenized specimen was heated for 30 min. at the desired temperature.

## 2. RESULTS

The complete equilibrium diagram of the system copper-germanium is shown in Fig. 2, whilst Figs. 3 and 4 give the details of the complicated region from 20 to 30 at.-% germanium. The results may be considered under the following headings.

#### (a) The Liquidus

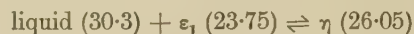
The liquidus point for alloy 12.40 † was found to lie within 1° C. of that given by the curve of Hume-Rothery, Mabbott, and Channel-Evans,<sup>1</sup> whose results for copper-rich alloys were therefore accepted and are included in Table I. The  $\alpha$  liquidus falls to a peritectic horizontal at 824° C., in reasonable agreement with the microscopical results of Hume-Rothery, Raynor, Reynolds, and Packer,<sup>4</sup> which placed the horizontal between 821.5° and 823° C. The compositions of the phases concerned correspond to the reaction:



From 824° C. the liquidus sinks to a eutectic horizontal at 743.5° C., in good agreement with the temperature bracket of 742°–743° C. obtained by Hume-Rothery *et al.*<sup>4</sup> At this temperature the liquid is in equilibrium with the  $\zeta$  and  $\epsilon_1$  phases, the compositions corresponding to the reaction:



The liquidus then rises to a very flat maximum at 747° C. and 23.5 at.-% germanium, and sinks gradually to a peritectic horizontal at 698° C., at which temperature the  $\eta$  phase is formed by the reaction:



The liquidus then falls steadily to a eutectic point at 644° C. and 36.5 at.-% germanium, at which temperature the liquid is in equilibrium with  $\eta$  (26.5) and almost pure germanium.

The present thermal analysis, in conjunction with the microscopical work referred to below, does not confirm the existence of the  $\gamma$  phase postulated by Weibke,<sup>8</sup> but does confirm the existence of a maximum on the liquidus, in contrast to the peritectic diagram of Schwarz and Elstner.<sup>9</sup> The existence of the  $\eta$  phase of Betterton<sup>12</sup> is confirmed, but the thermal analyses in this region are complicated by the fact that, apart from the eutectic horizontal at 644° C. referred to above, the  $\eta$  phase (see Fig. 3) undergoes a eutectoidal decomposition at 614° C., whilst at 636° C. there is a peritectoid horizontal at which the  $\eta$  and  $\epsilon_1$  phases react to form the  $\epsilon$  phase. In the present work these different arrests were clearly distinguished, but with more rapid rates of cooling this may not be possible. The relations between the  $\epsilon$  and  $\epsilon_1$  phases are described below.

The freezing point of germanium was previously thought to be 960° C., but recent authors<sup>15</sup> have given values between 936° and 940° C., although even as late as 1952, Wittig<sup>16</sup> determined the temperature as 959° C. The value of 937.5° C. was found in the present work. A spectrographic analysis of the resulting ingot showed the purity to be the same as that of the original material, which confirms that the precautions taken to avoid contamination were effective.

#### (b) The $\epsilon_1$ Phase

The composition limits within which this phase is stable were determined by the examination of more than

\* When silica tubes were used they were broken with a pestle on entering the quenching bath.

† For brevity, alloys are referred to by their atomic percentages

of germanium so that, for example, alloy 12.40 means an alloy containing 12.40 at.-% germanium.



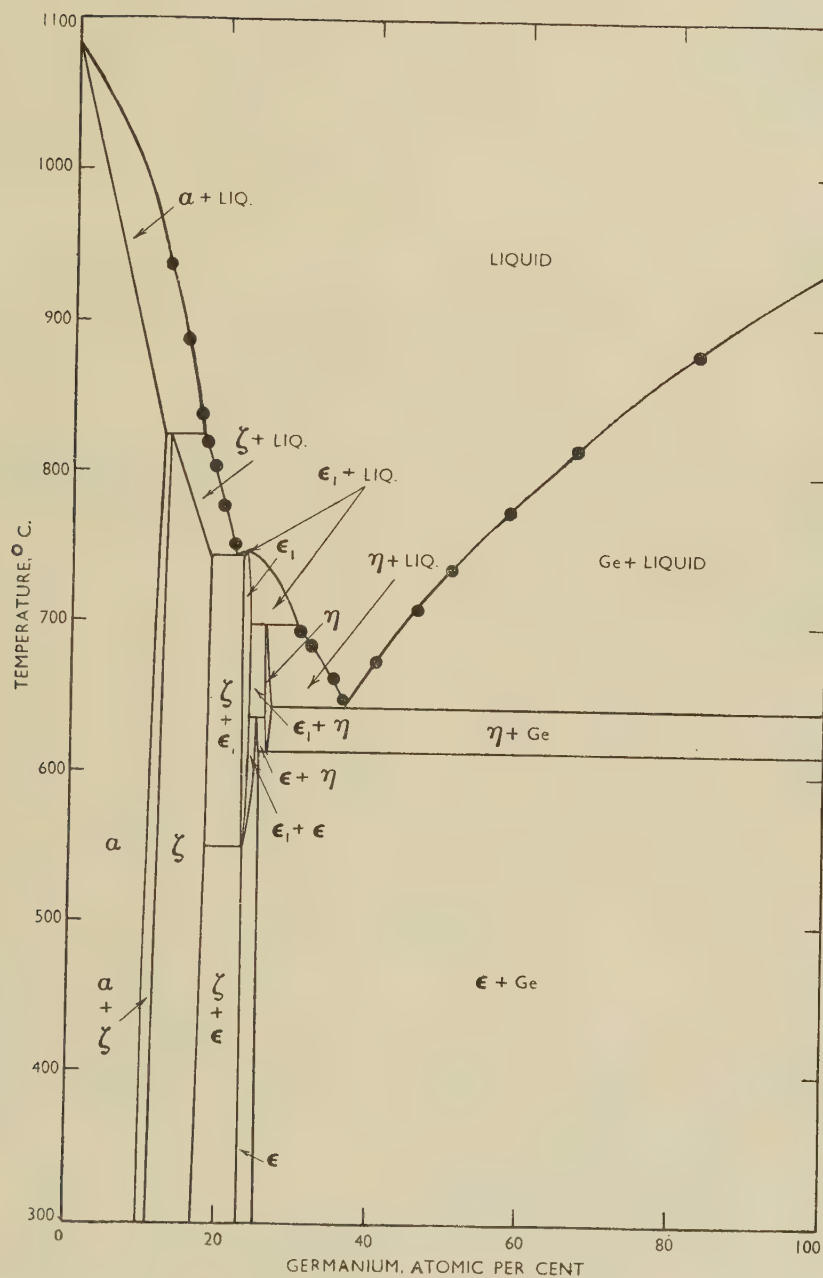


FIG. 2.—The Equilibrium Diagram of the System Copper-Germanium. (Present work.) The arrest points in the region 22-30 at.-% are omitted for clarity.

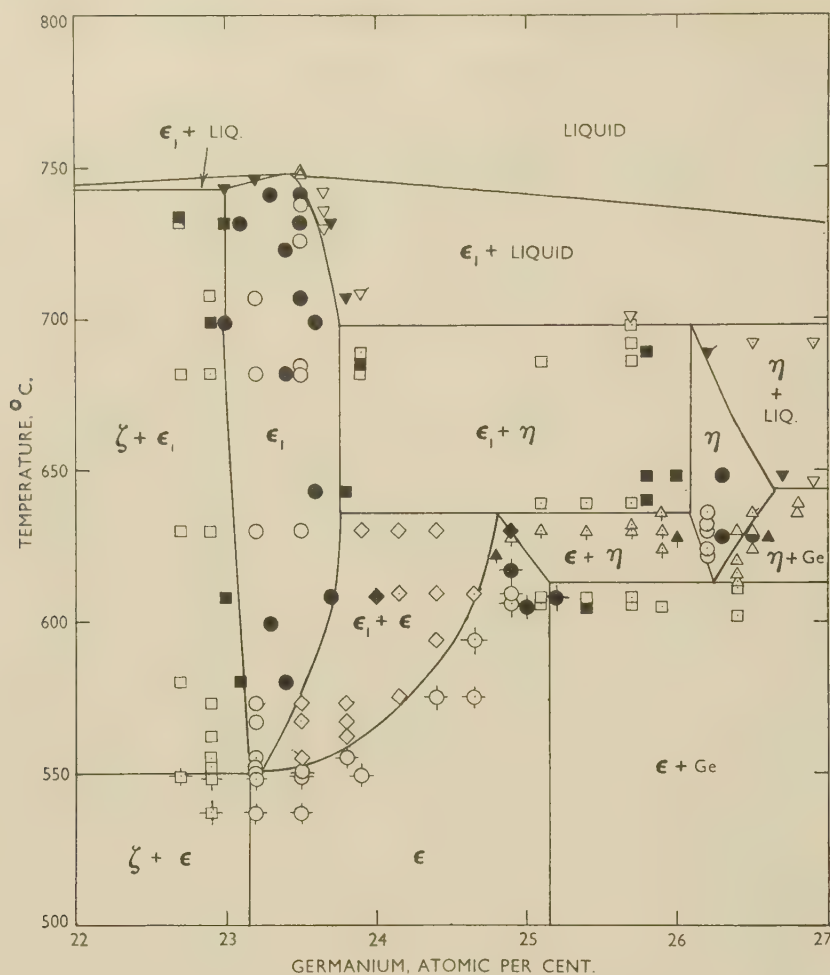
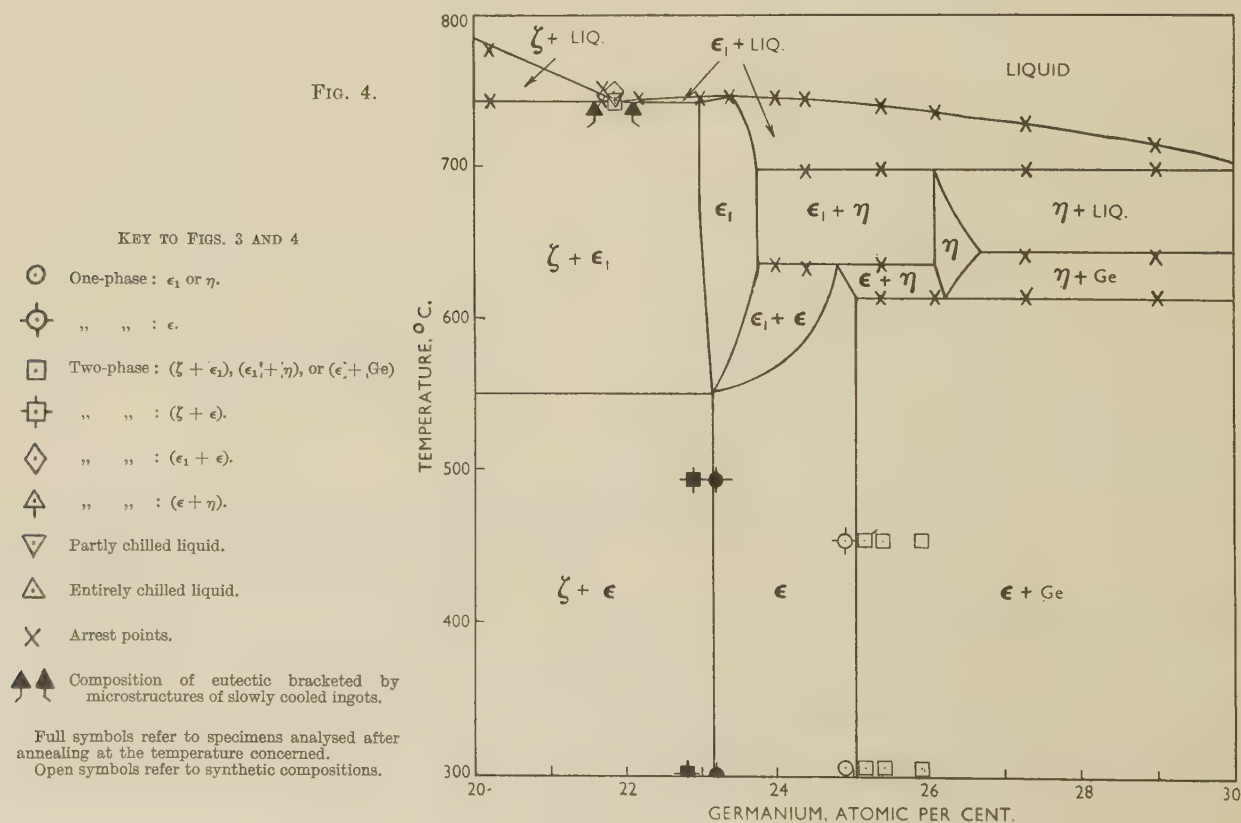


FIG. 3.

FIGS. 3 and 4.—The Equilibrium Diagram of the System Copper-Germanium in the Region 20-30 at.-% Germanium.



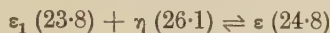


50 specimens annealed at the temperatures concerned, with the results shown in Fig. 3. The range of composition lies within the limits 23.0 and 23.8 at.-% germanium, and the maximum on the liquidus curve at 23.5 at.-% germanium is established conclusively as not corresponding with the ratio  $\text{Cu}_3\text{Ge}$ . At 549.5° C. the  $\epsilon_1$  phase undergoes transformation\* into the  $\epsilon$  phase, and the compositions of the two phases lie so close together that it was not possible to determine whether the transformation involves a peritectoid or a eutectoid reaction; in Fig. 3, the two phase fields are shown as meeting at the same composition (23.1 at.-% germanium).

Both the  $\epsilon_1$  and the  $\eta$  phases decompose on quenching, and some of the structures observed are described in Section 3 below.

#### (c) The $\epsilon$ Phase

The  $\epsilon$  phase field lies between the limits 23.0 and 25.1 at.-% germanium, and rises to a maximum at 636° C., the temperature of the peritectoid reaction:



The data could probably be reconciled with the simple whole-number ratio  $\text{Cu}_3\text{Ge}$  for the  $\epsilon$  phase. The  $\epsilon/\epsilon + \text{Ge}$  boundary is almost vertical. In annealed two-phase alloys lying slightly outside the boundary, the germanium is present in the form of small crystals, as shown in Fig. 5 (Plate XXI). As previously stated, in determining this boundary, it is important not to give preliminary annealing treatment above the temperature (613.5° C.) of the  $\eta$  eutectoid, because this results in the formation of comparatively coarse two-phase ( $\eta + \epsilon_1$ ) or ( $\eta + \epsilon$ ) alloys in which considerable diffusion is required to produce a uniform structure on annealing at lower temperatures. The  $(\zeta + \epsilon)/\epsilon$  boundary is nearly vertical. In two-phase alloys, the  $\zeta$  phase etches golden yellow, whilst the  $\epsilon$  appears white or light blue. The limits of the  $\epsilon$  phase-field were determined by the examination of 44 specimens. In Fig. 3, which is on a large scale, the most probable phase boundaries have been drawn. It will be seen that at the apex of the  $\epsilon$  phase field, alloy 24.9 is shown as lying on the  $\epsilon/(\epsilon + \eta)$  boundary, although its microstructure was recorded as ( $\epsilon + \epsilon_1$ ); whilst alloy 24.8, whose microstructure was ( $\epsilon + \text{trace of } \eta$ ), is placed within the homogeneous  $\epsilon$  field. The errors of composition involved are 0.1 and 0.2 at.-%, respectively, and it is not possible to say whether the discrepancies are due to slightly uneven composition or to errors in analysis.

#### (d) The $\eta$ Phase

The composition limits of this phase lie between 26.1 at.-% germanium at the 698° C. peritectoid horizontal, and 26.65 at.-% germanium at the ( $\eta + \text{Ge}$ ) eutectic horizontal, whilst the composition at which it decomposes eutectoidally is 26.25 at.-% germanium. The phase field was established by the examination of 50 specimens; the work was rendered very difficult owing to the occurrence of the curious decomposed structures referred to below. It is to be noted that the heating

curve of alloy 26.13 showed no arrests corresponding to either the 636° C. peritectoid or the 643° C. eutectic horizontal, thus confirming the microscopical work. In Fig. 3, alloy 26.5, which was described as homogeneous, lies outside the most probable phase boundary by 0.05 at.-%; this discrepancy is of the order of the experimental error. Some microstructures suggested that the limiting composition of the  $\eta$  phase at the eutectic horizontal was very slightly to the copper-rich side of that shown in Fig. 3. The  $\eta/\eta + \text{Ge}$  boundary would then be more nearly vertical, but this could not be conclusively established. The difference is slight.

#### (e) The Germanium Phase

The results of previous investigations were accepted as showing only an extremely small solubility of copper in germanium, and the microstructures indicated that no phases existed between the  $\epsilon$  and  $\eta$  phases and the germanium phase.

### 3. THE STRUCTURES OF DECOMPOSED $\epsilon_1$ AND $\eta$ PHASES

Both the  $\epsilon_1$  and  $\eta$  phases decompose on quenching, and the microstructures observed depend greatly on the rate of cooling. With very rapid quenching, the  $\epsilon_1$  phase gives rise to banded structures such as that of Fig. 6 (Plate XXI), which shows the structure of alloy 24.0 quenched from just above the solidus curve. The  $\epsilon$  phase does not decompose in this way, and this permitted the establishment of the small ( $\epsilon + \epsilon_1$ ) two-phase field by means of structures such as that of Fig. 7 (Plate XXI). With slower rates of cooling, the structure of decomposed  $\epsilon_1$  phase is much less definite, and examples such as those shown in Figs. 8 and 9 (Plate XXI) are observed.

The  $\eta$  phase also decomposes on quenching, and the confusing structures obtained are thought to be the result of two distinct processes. One type is associated with the eutectoid decomposition ( $\eta \rightleftharpoons \epsilon + \text{Ge}$ ), which cannot be suppressed by quenching, and gives rise to a structure of very small particles, such as those seen between the white needles in Fig. 10 (Plate XXI). The second type of structure is associated with the fact that in alloys lying on the copper-rich side of the  $\eta$  eutectoid, deposition of pro-eutectoid  $\epsilon_1$  or  $\epsilon$  phases occurs during quenching. With rapid rates of cooling, the pro-eutectoid phase separates in the form of thin plates, such as those shown in Fig. 10, and in a two-phase ( $\epsilon_1 + \eta$ ) alloy it is possible to distinguish between these plates and the  $\epsilon$  particles which are present at the quenching temperature. But with slower rates of quenching, this distinction is extremely difficult, and it is perhaps this fact which has led to confusion in the older diagrams.

### III.—DISCUSSION

The present work confirms the general form of the diagram proposed by Schubert and Brandauer<sup>13</sup> for the region 20–40 at.-% germanium, but the phase boundaries of the  $\eta$ ,  $\epsilon$ , and  $\epsilon_1$  phases lie at germanium contents

\* This expression is used for convenience. If the transformation is eutectoidal, the  $\epsilon_1$  phase will decompose at 549.5° C. into a mixture of  $\zeta$  and  $\epsilon$ . If there is a peritectoid horizontal,

there will be a minimum in the  $\epsilon_1/(\epsilon_1 + \epsilon)$  and  $\epsilon/(\epsilon_1 + \epsilon)$  boundaries at a temperature slightly different from 549.5° C.

higher by 1–2 at.-%. It is possible that this difference is the result of loss of germanium during the annealing of the filings or powder used in the X-ray work of the German investigators.

Fig. 11 shows the equilibrium diagrams of the systems copper-silicon and copper-germanium, and the general correspondence is remarkable. In each system the complicated sequence of solid phases is confined to the first 27 at.-% of the tetravalent solute, whilst the liquidus curves corresponding to the deposition of almost pure germanium and pure silicon penetrate far into the diagrams and end in eutectics. In each system there is a maximum in the liquidus curve at approximately 24

copper-germanium the range of composition 11–19 at.-% germanium is occupied by the one close-packed hexagonal  $\zeta$  phase. In the system copper-silicon almost exactly the same range of composition is occupied by the  $\kappa$ ,  $\beta$ ,  $\delta$ , and  $\gamma$  phases; there is general agreement that the  $\kappa$  phase is close-packed hexagonal, whilst the  $\gamma$  phase has the structure of  $\beta$ -manganese and occurs at almost exactly the characteristic electron concentration of 1.5.

The copper-silicon  $\eta$  and  $\eta_1$  phases occupy similar composition ranges to the copper-germanium  $\epsilon_1$  and  $\epsilon$  phases. In each case there is a high- and low-temperature modification whose composition ranges overlap, and the high-temperature modifications give rise to maxima

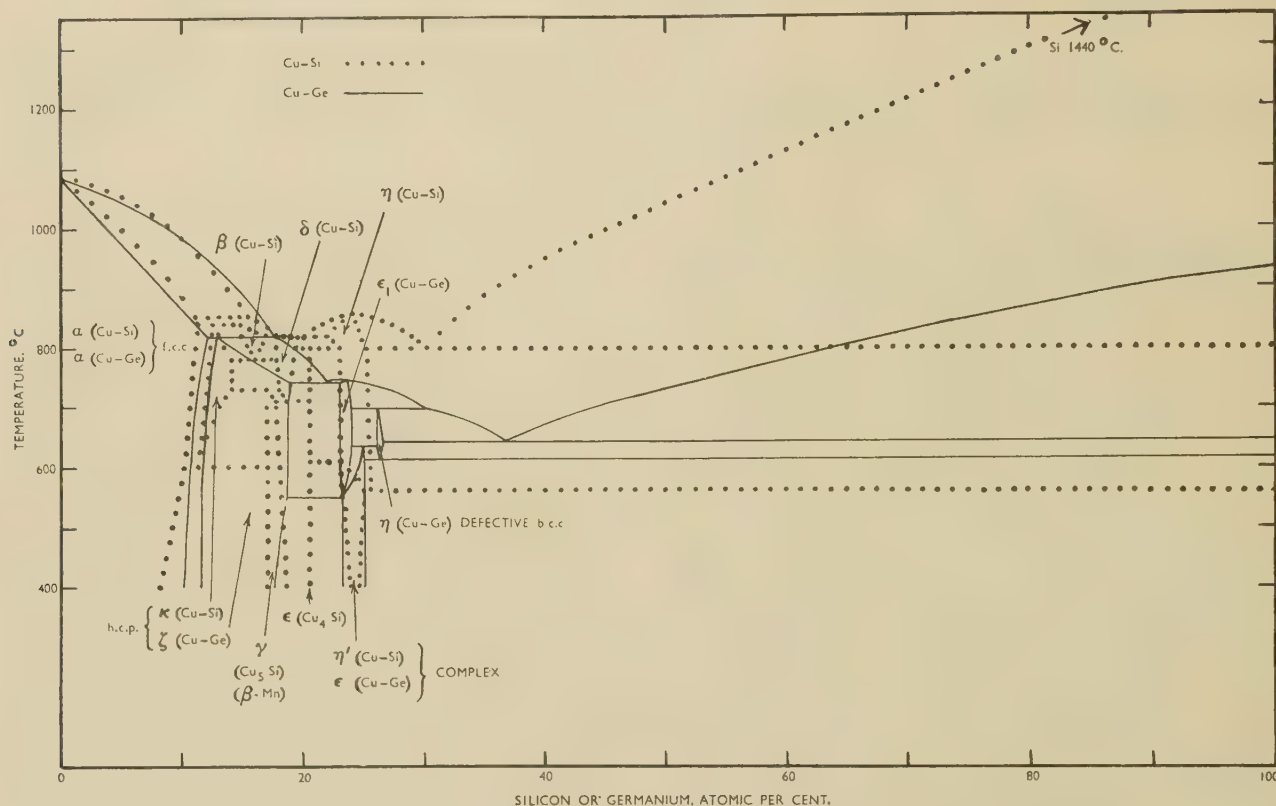


FIG. 11.—Comparison of the Equilibrium Diagrams of the Systems Copper-Germanium and Copper-Silicon.

at.-% of solute. This maximum is more pronounced in the system copper-silicon, in agreement with the more electronegative nature\* of silicon as compared with germanium.

The crystal structures of the phases in the system copper-silicon are incompletely known, but some resemblances to those of the system copper-germanium are apparent. The extents of the  $\alpha$  copper-silicon and  $\alpha$  copper-germanium primary solid solutions are of the same order. The  $\kappa$  copper-silicon phase has a close-packed hexagonal structure, and its copper-rich boundary coincides almost exactly with that of the  $\zeta$  copper-germanium phase of the same structure. In the system

on the liquidus curves at almost the same composition. A detailed investigation of the crystal structures of these phases would clearly be of interest.†

The copper-germanium  $\eta$  phase with a defect body-centred cubic structure does not find a counterpart in the system copper-silicon, but appears at almost the same electron concentration as that of the copper-zinc  $\delta$  phase which also has a defect body-centred cubic structure. In the system copper-gallium the corresponding range of composition (in electron concentration) is occupied by a defect modification of the  $\gamma$ -brass structure, which is itself a distorted defect modification of the body-centred cube. It is thus of great interest to see

\* The tendency for maxima of this kind to be more pronounced with increasing difference in the electrochemical characteristics of the two metals was first pointed out by Hume-Rothery, Reynolds,

Raynor, and Packer.<sup>4</sup>

† Schubert and Brandauer<sup>13</sup> have discussed these structures, but the details are not yet established.



how, in the system copper-germanium, where no phase with a  $\gamma$ -brass structure exists, a defect modification of the body-centred cubic structure reappears.

## ACKNOWLEDGEMENTS

The authors must express their gratitude to Professor Sir Cyril Hinshelwood, F.R.S., and to Dr. F. M. Brewer for laboratory accommodation and many other facilities which have greatly encouraged the present research. Thanks are also due to the Council of the Royal Society, and to the British Non-Ferrous Metals Research Association for financial assistance. Dr. J. C. Chaston of Messrs. Johnson, Matthey and Co., Ltd., kindly supervised the chemical analyses.

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A. L. Dighton and H. A. Miley, *Trans. Electrochem. Soc.*, 1942, **81**, 321 (i.e. year, volume, page).

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C. Zener, "Elasticity and Anelasticity of Metals". 1948: Chicago (University of Chicago Press).

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(As recommended by the Abstracting Services Consultative Committee)

1. **Purpose.** The synopsis is not part of the paper; it is intended to convey briefly the content of the paper, to draw attention to all new information, and to the main conclusions. It should be factual.

2. **Style of writing.** The synopsis should be written concisely and in normal rather than abbreviated English. It is preferable to use the third person. Where possible use standard rather than proprietary terms, and avoid unnecessary contracting.

It should be presumed that the reader has some knowledge of the subject, but has not read the paper. The synopsis should therefore be intelligible in itself without reference to the paper; for example, it should not cite sections or illustrations by their numerical references in the text.

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It is sometimes valuable to indicate the treatment of the subject by such words as: brief, exhaustive, theoretical, &c.

The synopsis should indicate newly observed facts, conclusions of an

experiment or argument and, if possible, the essential parts of any new theory, treatment, apparatus, technique, &c.

It should contain the names of any new compound, mineral species, &c., and any new numerical data, such as physical constants; if this is not possible, it should draw attention to them. It is important to refer to new items and observations, even though some are incidental to the main purpose of the paper; such information may otherwise be hidden, though it is often very useful.

When giving experimental results the synopsis should indicate the methods used; for new methods the basic principle, range of operation, and degree of accuracy should be given.

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When a synopsis is completed, the author is urged to revise it carefully, removing redundant words, clarifying obscurities, and rectifying errors in copying from the paper. Particular attention should be paid by him to scientific and proper names, numerical data, and chemical and mathematical formulæ.



# PSEUDO-SUBGRAIN STRUCTURES ON ALUMINIUM SURFACES \*

1732

By N. C. WELSH,† B.Sc., Ph.D., MEMBER

## SYNOPSIS

A number of workers have reported periodic markings of spacing about  $0.1\ \mu$  on the surface of electropolished aluminium and its alloys. The present investigation was made to explore the possibility that the markings represent some regular incoherence in the grain structure of the metal.

High-purity annealed aluminium was electrolysed under conditions ranging from electropolishing to heavy anodic oxidation. Electron microscopy showed, in most cases, regular markings of diverse pattern and of spacing  $0.03$ – $0.3\ \mu$ . The patterns varied according to the electrolyte, the conditions of electrolysis, and the crystallography of the metal surface. In all cases the dominant factor controlling the surface morphology was the potential applied to the electrolyte cell. The spacing of the markings increased progressively as the potential increased, the upper limit being set by breakdown of the anodic barrier layer. The changes of pattern and spacing and their dependence on the electric field are incompatible with the concept of a subgrain structure. The postulate is made that the markings originate from a micro-etch process acting through, and controlled by, a disperse anodic film.

## I.—INTRODUCTION

ELECTRON-MICROSCOPE studies by Bucknell and Geach <sup>1</sup> and by Brown <sup>2</sup> led to the discovery of fine line markings on replicas from anodically polished aluminium. The lines, which could be interpreted as shallow steps or grooves in the metal surface, were equi-spaced at intervals of about  $1000\ \text{\AA}$ . They frequently resembled furrows in their parallel alignment, and changed direction from grain to grain. Brown <sup>3</sup> noted that some grains showed an "orange-peel" pattern, and globular markings,  $400$ – $800\ \text{\AA}$  in dia., were observed by Nutting and Cosslett.<sup>4</sup> Bucknell, Geach, and Welsh <sup>5</sup> later found that the parallel alignment of the "furrows" was preserved only over a limited range of orientation around the  $(110)$  pole, the lines invariably following the  $\langle 100 \rangle$  direction. The markings were first detected after polishing in a perchloric acid-alcohol mixture, but Bussy,<sup>6,7</sup> made similar observations using a perchloric acid-acetic anhydride bath.

The regular spacing and orientation of these surface markings suggest that the electropolishing process reveals an intrinsic block structure of the metal crystals. Thus, the spacing of the furrows led Brown <sup>3,8</sup> to suppose that they represent traces of latent  $(111)$  slip planes equivalent to the "elementary slip lamellæ" of Heidenreich and Shockley;<sup>9</sup> this identity is, however, precluded by the evidence that the lines have  $\langle 100 \rangle$  direction on planes of  $\{hk0\}$  form.<sup>5,7</sup> Bussy <sup>6</sup> noted that the periodicity is of the same order as the dimensions of the "mosaic" of disoriented blocks first postulated by Darwin <sup>10</sup> to account for the X-ray reflecting power of crystals, and this correlation, if valid, would be of much interest. Whilst subgrain formation in metals is now a well-recognized phenomenon, evidence of crystal imperfection afforded by micrographic methods has usually indicated much larger block dimensions. Thus, the domains in recrystallized aluminium revealed

by the etching technique of Lacombe and Beaujard <sup>11</sup> ranged up to several millimetres in size. However, Hunter and Robinson <sup>12</sup> recently described cellular patterns on aluminium chemically polished by the patent Alcoa Bright-Dip Process which indicated blocks of only  $2000$ – $10,000\ \text{\AA}$ , a size not greatly different from the spacing of the furrow-like structures.

If the surface markings do bear some relation to a subgrain structure of the metal, it is obviously desirable that their character should be fully investigated. On the other hand, little information is available regarding the topography of electropolished surfaces on this minute scale, and if the markings should characterize the electropolishing process only, it is also important that their nature and circumstances of formation be elucidated to avoid the danger of false interpretation. The present communication reports a detailed study of aluminium surfaces anodically treated in baths of widely differing composition and electrolytic behaviour. Fine periodic structures were usually observed, varying greatly in pattern but all apparently generically similar.

## II.—EXPERIMENTAL PROCEDURE

Samples of high-purity (99.99%), rolled and annealed aluminium sheet were anodically electrolysed under carefully controlled conditions in the various media described below. Unless specifically referred to, the cathode material was carbon. The electrode separation was fixed and the stirring rate was constant. Current was normally drawn from a full-wave rectified, unsmoothed, A.C. source, but certain experiments were repeated with D.C. from a battery.

With the specimen immersed in the electrolyte, the applied potential was increased to the desired value and maintained constant throughout the polishing period. In each electrolyte the current flowing through the circuit was mainly governed by the resistance of a barrier

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layer, representing the products of anodic dissolution, which rapidly formed on the metal surface. Under fixed potential the current fell to a constant minimum value as the anodic layer developed its equilibrium thickness. Specimens were not, in general, removed from the bath until steady-state conditions prevailed.

Replicas of the metal surface were then prepared for electron microscopy by anodic oxidation in disodium hydrogen phosphate solution,<sup>13</sup> the oxide films being subsequently stripped by the well-known amalgamation method.<sup>14</sup> This oxidation treatment, henceforth referred to as "anodizing", produced films having an intrinsic structure of minute pores 100–250 Å. in dia., which set a limit to the resolution of the replica technique. Before anodizing, many of the specimens were etched in Lacombe and Beaujard's reagent,<sup>11</sup> which gives etch pits of cubic form, suitable for orientation measurement, without attacking the general surface.

The rolled sheet was of good surface finish and in most cases required no further preparation. However, certain of the electrolytes investigated had negligible smoothing action, and before use the specimens were electropolished in a mixture of 1 part nitric acid : 4 parts methyl alcohol.<sup>15</sup> This bath, alone of those studied, was found to produce smooth surfaces, free from any small-scale structure, and will not here be described in detail.

Attention must be drawn to the form of specimen employed, as this had an important bearing on the electrolytic behaviour. Strips of metal were varnished, leaving only an area 1 cm. square exposed to the bath action. The strip edges were completely sealed off, preliminary study having shown that without this protection unstable anode conditions developed at comparatively low voltages and consistent results were not obtainable.

### III.—RESULTS

#### 1. THE PERCHLORIC ACID-ALCOHOL BATH

The electrolyte in use when the surface structures were first discovered was a standard electropolishing bath consisting of 1 part perchloric acid (60%) : 4 parts ethyl alcohol.<sup>16</sup> The characteristics of the bath are best illustrated by the voltage/resistance curves shown in Fig. 1, the resistance being calculated on the basis  $V/C$ , where  $V$  is the applied potential and  $C$  the current density. The resistance is due predominantly to the anodic barrier layer, and the ordinate of Fig. 1 may be regarded as the resistance of each square centimetre of anode surface under steady-state conditions. This increases with applied voltage up to a limiting value, beyond which the barrier layer is unstable and the current flow increases sharply.

Specimens were prepared at voltage intervals up to the breakdown limit and at temperatures ranging from  $-46^{\circ}$  to  $+36^{\circ}$  C. Polishing took place under all conditions, though in varying degree. It soon became evident that the furrow-like structure first reported<sup>1,2</sup> is only one of many patterns which the polished surface may acquire in this bath. The variation of pattern was two-fold in origin: (a) complete changes of structure associated with changes in the conditions of electrolysis; (b) modifications of pattern from grain to grain, related to the crystal orientation of the substrate (these being

identified by the geometry of the cubic etch pits formed in Lacombe and Beaujard's reagent). In category (a), three basic structural patterns could be recognized, designated as "furrow", "dotted", and "globular" structures, which appeared under different regimes of applied potential and bath temperature. The regimes were not sharply defined, but were broadly as follows: 0–10 V., no detectable structure; 10–20 V., furrow structure; 20–30 V., a transition range from furrow to dotted structures; 30 V. up to the breakdown limit,

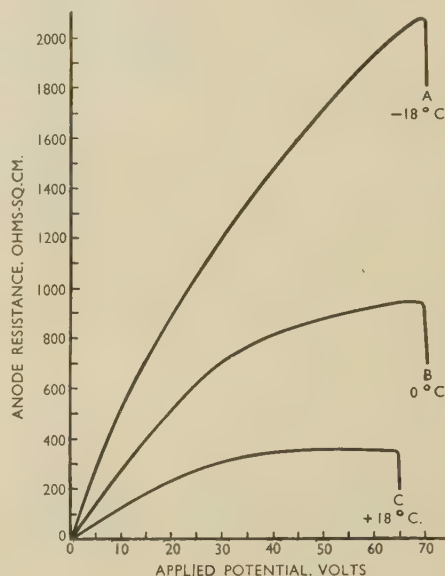


Fig. 1.—Voltage/Resistance Curves for the Perchloric Acid-Alcohol Bath.

dotted or globular structures, the latter appearing only at temperatures below  $0^{\circ}$  C. and potentials exceeding about 40 V. These structures are briefly described below and illustrated in Figs. 7–13 (Plate XXII).

#### (a) Furrow Structure

The regular line markings of the furrow structure are apparent in Fig. 7. It will be noted that they do not pass through the cubic etch pit introduced *after* electropolishing. On faces of near-(110) orientation (as Fig. 7) the lines were, with minor imperfection, constant in direction ( $\langle 100 \rangle$ ) across the grain, but as the orientation changed towards the (100) or (111) poles, less regular patterns developed. On near-(111) faces, the furrows degenerated into rows of granules; in Fig. 8 the linear arrangement has almost disappeared. In Fig. 9, which shows a ternary boundary, the furrow direction is constant on two of the grains, but varies greatly from point to point on the third. This maze-like pattern was characteristic of grains having orientation near to (100), though the granular pattern of octahedral faces (Fig. 8) sometimes also appeared on cube faces. A stereographic plot showing the range of orientation over which the furrows were straight and parallel has been published elsewhere.<sup>5,7</sup>

The oxide replicas are of the constant-thickness type, and change of contrast in the photographs represents a change of slope on the replicated surface. The furrow structure is constructed from narrow dark bands representing steep slopes, alternating with broad bands of



relatively shallow slope. Two possible replica profiles which would give this contrast scheme are shown in Fig. 2 (a) and (b); but direct observation of curled-up replica edges indicated (b) to be the general contour form.

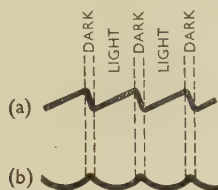


Fig. 2.—Replica Contours giving Observed Contrast Scheme.

The constancy of direction and spacing of the furrows on near-(110) faces was striking. It is significant that the perfection of the structure was not detectably affected by heavy cold working of the metal before electropolishing, though even light deformation of the polished strip caused pronounced disregistry at lines of slip. If the furrows represent fixed traces of a block structure of the metal, disruption of the blocks by cold working would be expected to show corresponding disorder in the symmetry of the furrows.

#### (b) Dotted Structure

The change from furrow to dotted structure took place progressively as the voltage increased, the lines breaking up into arrays of discrete dots, each dot representing a minute asperity. Fig. 10 (Plate XXII) shows an intermediate stage. On one grain short furrow lengths are separated by rows of dots; on the other the transition is complete. Fully dotted structures developed first on cube or octahedral faces, but at higher voltages the line structures disappeared completely, leaving dotted patterns with no clear relationship to the orientation of the substrate (Fig. 11, Plate XXII).

#### (c) Globular Structure

At high voltages and low temperatures of operation the dotted structure was replaced wholly or in part by an aggregate of globular markings, representing shallow, circular pits. In Fig. 12 (Plate XXII) the globules are closely stacked, resembling a bubble raft, but all degrees of dispersion down to isolated globules were encountered. The arrangement of Fig. 13 (Plate XXII) in which the globules are grouped mainly in clusters of three, suggests an element of symmetry, but the patterns showed no tangible relationship to the orientation of the metal.

These circular markings were easily distinguished from the modification of the furrow structure referred to as "granular" (see Fig. 8, Plate XXII). The term "granular" is used throughout to denote patterns in which the structural units were irregular polygons.

#### (d) Spacing of the Structures

The potential applied to the electropolishing cell appeared to be the dominant factor controlling not only the geometry of the surface patterns, but also the spacing of the structural units. The spacing between equivalent points of each pattern increased progressively as the applied potential increased. It is remarkable that, in spite of the differing character of the patterns, their periodicity changed in the same general manner illu-

strated by Fig. 3, where the mean structure spacings on a large number of specimens are incorporated regardless of pattern. The measurements were too numerous for individual plotting, but the vertical lines show the spread of results at various voltages. The spread is large, but the change of spacing with voltage is quite definite.

In constructing Fig. 3 no regard has been paid to the bath temperature or current density during polishing, as these variables had no detectable influence on the structure spacing. At constant voltage the bath temperature, and in consequence the current density (see resistance curves of Fig. 1), could vary widely without change of spacing. Nor was the time of polishing of significance, at least for periods greater than about 30 sec. The measurements shown apply to polishing times of 3–6 min., but periods of only a few seconds' duration gave smaller spacings. However, the first stage of polishing was one of instability, the voltage rising

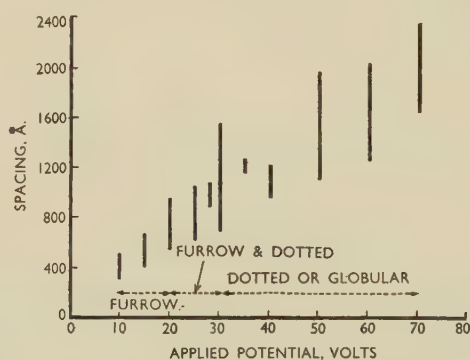


Fig. 3.—Voltage/Spacing Relationship for the Perchloric Acid-Alcohol Bath. Rectified A.C. specimens.

and the current falling to their equilibrium values as the anodic layer developed, and the lower voltages obtaining during this transition period probably account for the smaller spacings.

#### (e) Structureless Zones and Crystallographic Etching

It is apparent from Fig. 3 that the structures appearing at the lowest voltages were extremely fine, approaching the resolution limit set by the inherent structure of the oxide replicas (250 Å.), and the absence of recognizable patterns on specimens electrolysed at potentials of less than 10 V. may simply indicate inadequate resolution. However, structureless zones also appeared at voltages approaching the breakdown limit, though replicas devoid of all structure were rarely observed. Structure disappeared selectively from different crystal faces (see Fig. 11, Plate XXII), the number of structureless grains increasing as the voltage increased. Simultaneously with the loss of structure, there appeared a form of crystallographic etching which yielded minute cubic etch pits varying in size from about  $1\mu$  down to the minimum detectable. The pits usually formed on otherwise structureless grains (Fig. 14, Plate XXII), but were occasionally superimposed on dotted or globular structures; thus many of the globules in Fig. 13 (Plate XXII) have minute etch pits attached. The proportion of the grains affected increased with voltage and, like the loss of general surface structure, this form of etching seemed to foreshadow the disintegration of the anodic barrier layer.

## (f) Direct-Current Polishing

The morphology of the polished surface was clearly determined by the electrolytic conditions, and to establish whether the nature of the power supply is of consequence, a number of specimens were prepared by using D.C. from a battery source. The applied potential could now be increased to 95–100 V. before breakdown occurred, compared with only about 70 V. for rectified A.C. at the same temperature (0° C.), suggesting that the peak voltage, i.e.  $\pi/2 \times$  the average value, was determining the breakdown limit in the latter case.

In Fig. 4 the spacings of the structures observed are

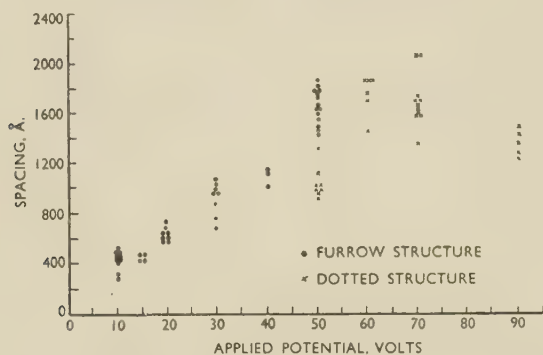


Fig. 4.—Voltage/Spacing Relationship for the Perchloric Acid-Alcohol Bath. D.C. specimens.

shown, each point representing the mean spacing on a single grain, and the code indicates the relevant structural pattern. The voltage range within which furrow-type structures appeared is seen to extend up to about 50 V., compared with only 30 V. for rectified current. This difference, as with the breakdown limit, may be associated with the difference between peak and average value of voltage. The structures show the same general increase in spacing up to 70 V., as did the rectified-current specimens, though measurements on a single specimen polished at 90 V. did not maintain the increase. The results strongly reinforce the conclusion that the potential applied during electropolishing is the dominant factor determining the size and pattern of the surface structures.

## 2. THE PERCHLORIC ACID-ACETIC ANHYDRIDE BATH

The electropolishing bath developed by Jacquet<sup>17</sup> consisting of 215 c.c. perchloric acid and 785 c.c. acetic anhydride, was not studied in detail. However, Bussy<sup>6,7</sup> has described structures on aluminium and its alloys polished in this electrolyte which closely resemble those under consideration. He found that the structure spacings on a large variety of specimens gave a mean value almost invariably within 10% (the approximate error of measurement) of 1000 Å. The constancy of spacing favoured the hypothesis that traces of a block structure of the metal were being revealed, but the electropolishing conditions were not stated. It seemed improbable that the wide changes of spacing observed in the perchloric acid-alcohol bath would not recur in this electrolyte, and in the present work a series of specimens were prepared at various voltages and a bath temperature of 18° C. The structural patterns and spacings found were as follows:

10 V.: No detectable structure.

15 V.: Granular on cube faces but furrow pattern on grains of near-(110) orientation. Spacing 660–770 Å.

20 V.: Same as 15 V. Spacing 960–1290 Å. (Fig. 15, Plate XXII).

40 V.: Granular on all crystal faces. Spacing 1150–1500 Å.

50 V.: Same as 40 V. with fine-scale etching. Spacing 1720–2300 Å. (Fig. 16, Plate XXIII).

The structure spacing thus varied from about 700 to over 2000 Å. on increasing the applied voltage from 15 to 50 V., a change far beyond possible error of measurement. The constancy of Bussy's measurements is thus misleading and due, probably, simply to constancy of voltage during electropolishing. At a given voltage the spacings compare favourably with those determined for the perchloric acid-alcohol bath, and there can be no reasonable doubt that the cause of structure formation is the same for both electrolytes.

## 3. SIGNIFICANCE OF THE STRUCTURES

The variable patterns and spacings of the markings found in the perchloric acid baths were incompatible with the concept of a block structure of the metal and must, it seemed, originate from surface phenomena involved in the electropolishing process itself. The mechanism of electropolishing is still imperfectly explained, but, in general terms, the smoothing action is supposed to result from the shielding effect of the products of anodic reaction, viz. the anodic barrier layer. The layer is usually regarded as a viscous liquid of high resistance, thick in the hollows and thin at asperities, the consequent disparity in current density promoting the levelling action. However, the converse should also hold true, i.e. that discontinuities in the anodic film would lead to roughening of a smooth surface. On the scale of the surface irregularities under consideration, the film is not necessarily homogeneous. The period of the structures, 250–2500 Å., is of colloid dimensions, and the possibility was envisaged that the primary patterns were those of a disperse anodic phase, the patterns being transferred to the metal surface by a micro-etch process proceeding simultaneously with the overall smoothing action.

Although resistance measurements left no doubt as to the reality of the barrier layer during electropolishing in the perchloric acid baths, the anodic reaction does not produce a permanent surface film. Subsidiary experiments showed in fact that the barrier layer is immediately destroyed on lifting the specimen from the electrolyte; on re-immersion, the current flow temporarily rises to the high value characteristic of the first stage of polishing. It seemed pertinent to enquire whether similar surface patterns develop under conditions such that the barrier layer consolidates as a stable oxide film—conditions which are realized in the phosphoric acid and hydrofluoric acid baths described below.

## 4. THE PHOSPHORIC ACID-ALCOHOL-WATER BATH

Larke and Wicks<sup>18</sup> have suggested a bath for polishing aluminium consisting of 400 c.c. phosphoric acid (sp. gr. 1.75), 380 c.c. ethyl alcohol, and 200 c.c. water. A potential of 27–30 V., bath temperature of 40° C., and an aluminium cathode are recommended. The authors state that low current densities or temperatures cause anodic-film formation.

Replicas from surfaces electropolished in this bath



under the prescribed conditions showed clear granular structures of the same size-order as the patterns of the perchloric acid bath, but similar structures were found to develop at lower temperatures when even prolonged electrolysis had little brightening action. The main study was made at 18° C., at which temperature adherent oxide films form on the metal surface. Very low current densities were recorded until the potential exceeded about 90 V., when breakdown occurred and high, unstable currents passed. The form of the voltage/resistance curve is shown in Fig. 5. The curve has a maximum at about 50 V., but at all voltages the resistances are much greater than for perchloric acid-alcohol polishing (cf. Fig. 1, curve C).

Further treatment in the anodizing bath yielded replicas too thick for electron microscopy, and before replication most of the specimens were deoxidized in an aqueous solution containing 2% chromic acid: 4% phosphoric acid, held at 70° C.<sup>19</sup> In some cases, however, the anodizing treatment was omitted, and the oxide film produced during electrolysis was itself stripped by the mercury method. Although these films were almost opaque to the electron beam, a pore structure was clearly visible in them, corresponding in pattern and

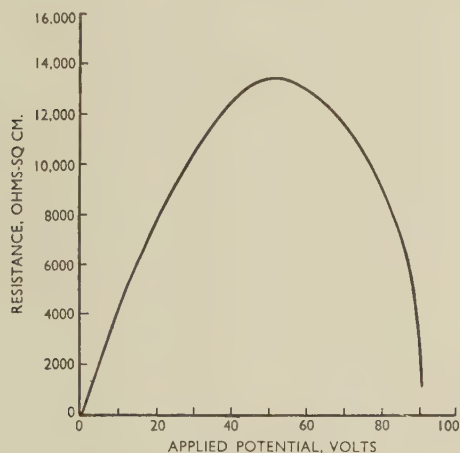


FIG. 5.—Voltage/Resistance Curve for the Phosphoric Acid-Alcohol-Water Bath (18° C.).

size to the structures on deoxidized surfaces (Figs. 17 and 18, Plate XXIII).

#### (a) Voltage-Dependence of Structure

Over the whole voltage range up to the breakdown limit, granular structures were observed on the metal surface (Figs. 19–21, Plate XXIII). The granules were randomly packed, and though they varied appreciably in size from grain to grain, the variations showed no consistent relationship to the crystal orientation of the substrate. There was no change of structural pattern with orientation or with voltage equivalent to that found in the perchloric acid-alcohol bath. The average diameter of the granules did, however, vary widely and systematically with voltage, as shown in Fig. 6. It is apparent that in spite of the widely different characteristics of the baths and dissimilarity of structural pattern, the voltage/spacing relationship compares very closely with that for perchloric acid-alcohol polishing (cf. Fig. 3). The correspondence is too close to be

fortuitous, and clearly indicates that the fine structures developing in the two electrolytes are generically similar. In this case, however, structure formation took place beneath a visible anodic film which itself showed similar structural characteristics (Figs. 17 and 18, Plate XXIII).

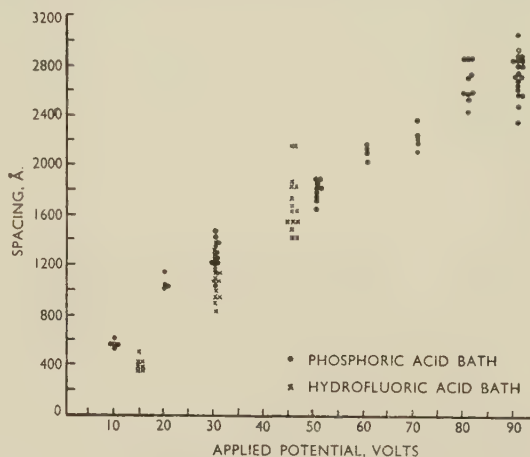


FIG. 6.—Voltage/Spacing Relationships for Phosphoric Acid and Hydrofluoric Acid Baths.

#### (b) Influence of Deoxidant

Although the chromic-phosphoric acid deoxidant rapidly attacked the oxide film formed during electrolysis, the replicas often showed evidence that a residue of the film had been picked up by the new film formed during anodizing. Thus, the cubic faces of etch pits (introduced after electrolysis but before anodizing) were normally structureless, but occasionally showed signs of the same granular structure as was present on the general surface. Fig. 20 (Plate XXIII) reveals the explanation for this spurious etch-pit structure. An etch-pit has broken away from the replica, but traces of a second film can be seen extending across the gap. The structure visible in the gap is believed to represent that of the oxide film in most intimate contact with the metal during electrolysis.

The chromic-phosphoric acid mixture did not attack the metal surface unless the solution-treatment was greatly prolonged, but an alternative deoxidant, an aqueous 1% hydrofluoric acid solution, did rapidly etch the metal. Fig. 21 (Plate XXIII) is typical of specimens deoxidized in the latter solution. The granular structure is still clearly visible, but the granules have acquired facets, probably (100), which give them a different appearance on different crystal faces. It is certain that this facet development is characteristic of the deoxidant and not of the electrolytic treatment. The effect is of particular interest in the present context by demonstrating the manner in which a surface-etching process may be controlled by the presence of a cellular oxide film.

#### (c) Structures Beyond the Breakdown Limit

Specimens were not normally prepared beyond the breakdown limit, owing to the serious heating effects of the heavy currents. In a few cases, however, the voltage was increased beyond the limit and then reduced to 50–60 V., the turbulence preventing layer formation and maintaining high current densities. The structures

on such specimens did not correspond to those found at the same voltage before breakdown, and varied from point to point on the replica. Some areas were structureless, others showed irregular markings or granular structures of diverse form. One example is shown in Fig. 22 (Plate XXIII). The fact that the structures varied widely over short distances is significant. The anode resistance after breakdown was only about 20 ohms-cm.<sup>2</sup>, compared with about 12,000 ohms-cm.<sup>2</sup> at the same voltage before breakdown. If, as suspected, the structures are determined by the constitution of the barrier layer, uniform structures would not be expected under conditions when the latter is patently unstable.

#### 5. THE HYDROFLUORIC ACID-ALCOHOL-WATER BATH

In contrast to the previous bath, which, although designed for electropolishing, is strongly oxidizing under some conditions, the electrolyte consisting of 2% hydrofluoric acid, 49% ethyl alcohol, 49% water,<sup>20</sup> was developed specifically as an oxidizing bath for aluminium and has negligible polishing action. Thick oxide films grown in this bath, as in certain other electrolytes,<sup>21, 22</sup> have a striated appearance due to parallel grooves, several microns in spacing, which form on the outer surface. The grooves change direction from grain to grain and are related in some way, not fully elucidated, to the orientation of the substrate. The striæ were found to have  $\langle 100 \rangle$  direction,<sup>23</sup> i.e. the same directionality as the furrow-type structure of the perchloric acid bath, though the spacing of the latter is very much smaller. It seemed reasonable to suppose that the oxide striæ would be associated with equivalent structure at the metal interface. This proved to be the case.

Fig. 23 (Plate XXIII) shows the structure of a specimen electrolysed at 45 V., 18° C., and deoxidized before replication. A cellular structure is apparent, resembling that obtained in the phosphoric acid bath (cf. Fig. 20, Plate XXIII), but in this case the cells show a definite linear arrangement on near-(110) faces. The lines again have  $\langle 100 \rangle$  direction, but the spacing is less regular than for the furrow-type structure (cf. Fig. 7, Plate XXII). Relationship with the structures earlier described was confirmed by spacing measurements at various voltages. The measurements are shown, along with those for the phosphoric acid bath, in Fig. 6, and the correspondence is immediately apparent.

Attention must, however, be drawn to an unusual type of marking found in this bath when operating at a potential of only 5 V. Such specimens were usually structureless, but occasionally replicas showed the comparatively coarse cell structure of Fig. 24 (Plate XXIII). These markings were not observed on higher-voltage specimens and represent a quite distinct phenomenon, involving direct etching of the metal in the absence of a thick, protective barrier layer. Similar, though often more intricate, patterns were found to develop on long immersion of the metal without applied e.m.f. in several of the electrolytes used in this work; these resembled in many cases the markings found by Hunter and Robinson<sup>12</sup> on chemically polished aluminium. The significance of these coarser structures, which may, as the latter authors claim, truly represent some fundamental structure of the metal, will be separately discussed elsewhere.

#### IV.—DISCUSSION

The primary object of the present investigation was to examine the possibility that the surface markings are traces of an internal structure of the metal. Very strong evidence has been obtained to refute this notion. Genuine subgrain structures are known to vary in size according to the purity, deformation, and thermal history of the metal, but, allowing for such variations, the shape and size of subgrain blocks are fixed. The present structures, on metal of constant purity and history, could be controllably varied in both size and pattern simply by adjusting the conditions of electrolysis, and it is impossible to reconcile these variations with the concept of a three-dimensional block array within the metal. The size-factor alone could be varied as much as tenfold, the upper size limit in each electrolyte being determined by the breakdown voltage of the anodic layer. Consideration of the actual geometry of the structural units provides another formidable obstacle to the subgrain hypothesis. Whereas the granular patterns of the phosphoric bath (Figs. 19–21, Plate XXIII) might conceivably be traces of more or less equiaxed subgrain blocks, the furrow pattern obtained in the perchloric acid baths (Figs. 7, 9, and 15, Plate XXII) would indicate asymmetrical blocks. Moreover, the furrow pattern on (110) faces suggests an array of equi spaced, rod- or plate-like blocks with long axes in the cube direction, but neither configuration would be expected to yield on cube and octahedral faces the patterns observed (see Figs. 7–9, Plate XXII). The dotted structure found in specimens treated in the same bath at higher voltages (Figs. 10 and 11, Plate XXII) is not indicative of any closed-cell substructure, and the globular structure (Figs. 12 and 13, Plate XXII) would again suggest equiaxed blocks.

The directional character of the furrow-type structure makes it tempting to suppose, as did Brown,<sup>3, 8</sup> that an analogy may be drawn with the much coarser and less-regular striæ which develop on certain metals heated to high temperatures in mildly oxidizing atmospheres. The cause of striæ formation during thermal etching has not been established with certainty, but it probably involves one or both of two mechanisms: (a) selective oxidation of certain crystal planes and evaporation of the oxide molecules;<sup>24</sup> (b) reorganization of the profile to a configuration of minimum free energy by surface migration of metal atoms.<sup>25, 26</sup> It seems unlikely that, at the low temperatures of electrolysis, surface migration of atoms could effect appreciable change in the surface topography, but, analogously to mechanism (a), the electrolytic structures might develop by preferred oxidation of certain crystal planes and solution of the oxide in the electrolyte. However, many of the patterns showed no obvious relationship to the crystallography of the substrate and cannot readily be accounted for on this basis; nor is the controlling influence of the applied electric field explained in this way.

The dominant effect of the electric field on the geometry and spacing of the surface patterns points to the anodic barrier layer as the seat of structure formation. The suggestion was made earlier that the patterns obtained in the perchloric acid baths reflect some regular incoherence in the constitution of the barrier layer. This postulate is greatly strengthened by the discovery



that equivalent patterns develop under oxidizing conditions in the phosphoric and hydrofluoric acid electrolytes. Here the anodic layer is manifest as an oxide film which itself shows a definite cellular structure (Figs. 17 and 18, Plate XXIII), and an intimate relationship with the corresponding patterns on the metal surface is readily inferred.

The porous character of anodic oxide films has been frequently noted, the work of Keller, Hunter, and Robinson<sup>27</sup> being of special interest in this respect. These authors studied the cellular structure of films grown in aqueous solutions of sulphuric, chromic, oxalic, and phosphoric acids and observed that the cell size increased linearly with voltage, the dimensions and shape of the cells closely paralleling those here found in the phosphoric acid electrolyte. A theory of cell formation is proposed. Pores are considered to develop in the oxide film by solvent action of the electrolyte, concentrating the current at these points. The oxide advances into the metal on a spherical front around each pore, the metal acquiring the scalloped contour of the cells thus formed. As the applied potential increases, the cell walls thicken (film thickness being a function of voltage<sup>28</sup>), causing an increase of cell size.

It is remarkable that the simple polygonal oxide cells studied by Keller, Hunter, and Robinson, like those given by the phosphoric acid electrolyte here described, should show the same voltage/spacing characteristics as the diverse patterns of the electropolishing baths (cf. Figs. 3 and 6), and a basic relationship between the structures must be inferred. This relationship might accordingly be interpreted as evidence that oxidation plays a major role in the electropolishing process. It is, however, difficult to explain the electropolishing patterns in terms of the theory of oxide-cell growth outlined by Keller, Hunter, and Robinson, which requires the existence of an oxide film of thickness comparable with the cell spacing. It is most improbable that solid films of equivalent thickness exist under electropolishing conditions. Thus the oxide films detected by Raether<sup>29</sup> on aluminium electropolished in various media were no more than a few tens of Ångströms thick, and there is doubt whether even such thin films exist during electropolishing or whether they form on subsequent contact with the atmosphere or the fluids used in washing. Moreover, as mentioned earlier (Section III, 3), the barrier effect in the perchloric acid-alcohol bath was destroyed by lifting the specimen from the bath and re-immersing, a fact suggesting that the resistance layer has the nature of a viscous liquid rather than a solid.

Reference may be made to Wernick's proposal<sup>30</sup> that during electrolysis a peptized gel of aluminium hydroxide forms a net-like sponge over the anode surface. This concept is in keeping with the notion of a liquid or semi-liquid film, and the possibility remains that under electropolishing conditions the primary discontinuities leading to accelerated local attack of the metal are determined by the intrinsic state of dispersion of the anodic phase (see Section III, 3), rather than by pores forming randomly in a continuous, solid film. Furthermore, the micro-etch process ultimately responsible for the morphology of electropolished surfaces (see Figs. 7-13, and 15, Plate XXII, Fig. 16, Plate XXIII) is clearly of much greater complexity than that prescribed by Keller, Hunter, and Robinson for oxide-cell growth.

A complete understanding of the anodic processes

leading to structure formation is not yet possible. Nevertheless, the evidence seems conclusive that the surface patterns develop independently of any internal imperfection which the metal crystals may contain and, in this respect, are simply artefacts. Only in one of the four electropolishing baths studied (the nitric acid-alcohol mixture) were structure-free surfaces produced. Since electropolishing is almost invariably a preliminary to electron-microscope studies of aluminium and its alloys, the present findings plainly emphasize the caution necessary in interpreting fine structures revealed by such means.

*Note added in Proof.*—Hulme<sup>31</sup> has recently described structures formed on zinc crystals during electropolishing, which resemble the "furrow" patterns on aluminium, though the spacing is much greater (1-6  $\mu$ ). Hulme likewise attributes the structures to the electrode process and not to a substructure of the crystals.

#### ACKNOWLEDGEMENTS

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# FLOW AND FRACTURE CHARACTERISTICS OF BINARY WROUGHT MAGNESIUM- LITHIUM ALLOYS\*

1733

By M. W. TOAZ, † M.Sc., and E. J. RIPLING, ‡ Ph.D.

## SYNOPSIS

The tensile properties of three extruded magnesium-lithium alloys, having respectively completely hexagonal (4% lithium), mixed hexagonal and cubic (6% lithium), and completely cubic (11% lithium) structures, are described as a function of testing temperature and strain rate. Each of the alloys displayed an embrittling temperature which was strain-rate sensitive. The embrittlement was most severe for the completely cubic alloy.

The mixed hexagonal and cubic, as well as the completely cubic alloy, yielded discontinuously over restricted temperature ranges. Two completely different types of discontinuous yielding were found in each of the alloys. At all strain rates and at all temperatures, with the possible exception of high temperatures, the hexagonal and the mixed hexagonal and cubic alloys developed transgranular cracks, apparently on twins, after rather small strains.

The completely cubic alloy formed premature intergranular cracks only under the testing conditions that produced low ductility. This might result from the localized diffusion of sodium to the grain boundaries.

## I.—INTRODUCTION

THE addition of about 10 wt.-% lithium to magnesium gives rise to highly workable, stable, body-centred cubic alloys in place of the normally rather brittle, hexagonal metal. For this reason the magnesium-lithium alloys have proved one of the most intriguing of the potential light-weight structural materials, as attested by the interest shown in these alloys by such outstanding early workers as von Zeppelin<sup>1</sup> and Hume-Rothery.<sup>2</sup> Although the binary alloys are hardly of practical interest,<sup>3</sup> additions of third elements can lead, through age-hardening, to alloys of extremely high strengths.<sup>4-5</sup> Since lithium is even lighter than magnesium, these multi-component systems frequently are lighter than magnesium itself, and are almost always lighter than the commercial hexagonal magnesium alloys.

Although the binary and some ternary equilibrium diagrams have been investigated with fair thoroughness, there are practically no data available on the mechanical properties of the binary magnesium-lithium alloys to serve as a basis for the intelligent design of the ternary or more complex alloys. § For this reason, the investigation described was undertaken to determine the tensile behaviour of a series of magnesium-lithium binary alloys at various strain rates and temperatures.

## II.—MATERIAL AND PROCEDURE

Three magnesium-lithium alloys, listed in Table I, were received as  $\frac{5}{8}$ -in.-dia. extruded rods. Their compositions were selected to correspond to a variety of

TABLE I.—Composition (Wt.-%) of Magnesium-Lithium Binary Alloys.\*

Element	Mg-4% Li	Mg-6% Li	Mg-11% Li
Li † . . .	3.6	5.8	10.6
Na † . . .	0.016	0.030	0.068
Al . . . .	0.0015	0.0015	0.0020
Ca . . . .	0.012	0.015	0.015
Cu . . . .	0.003	0.003	0.006
Fe . . . .	0.021	0.018	0.010
Mn . . . .	0.032	0.029	0.027
Ni . . . .	<0.001	<0.001	<0.001
Pb . . . .	<0.001	<0.001	<0.001
Si . . . .	<0.01	<0.01	<0.01
Sn . . . .	<0.01	<0.01	<0.01
Zn . . . .	<0.02	<0.02	<0.02

\* These alloys and the analyses were supplied by the Dow Chemical Company.

† Flame photometer; otherwise spectrographic.

structures: (a) the 4% lithium alloy consisted of a single hexagonal phase; (b) the 6% lithium alloy was a

\* Manuscript received 17 October 1955; in revised form 5 April 1956. The paper is based on a portion of a research programme conducted in the Department of Metallurgical Engineering, Case Institute of Technology, in co-operation with the Pitman-Dunn Laboratory of Frankford Arsenal.

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with the Continental Can Company.

§ Note added in proof: Subsequent to the acceptance of the present manuscript, a paper appeared in this *Journal* by Professor W. R. D. Jones, entitled "The Mechanical Properties of Binary and Ternary Magnesium Alloys Containing Lithium" (*J. Inst. Metals*, 1955-56, **84**, 364). In this paper, Professor Jones presented a considerable amount of data on the mechanical properties of as-cast and rolled magnesium-lithium (6½ and 12% lithium) alloys and magnesium-lithium-third-component alloys. Professor Jones's data do not, however, alter the conclusions of this paper.

two-phase structure (80% hexagonal and 20% body-centred cubic); (c) the 11% lithium alloy consisted of a single body-centred cubic phase. The microstructure and A.S.T.M. grain-size of each alloy are shown in Fig. 11 (Plate XXIV).

Unfortunately, the sodium content of the alloys increased as the lithium content was increased, so that the results presented may not be a unique function of lithium content and crystal structure.

Specimens of the type shown in Fig. 1 were rough machined from the as-received rods. They were then annealed\* for 1 hr. at 675° F. (355° C.), air-cooled, and final machined. Additional heat-treatments were given the 11% lithium alloy to alter its grain-size: grain refinement was produced by cold swaging rods 50%,† followed by annealing for 2 hr. at 500° F. (260° C.), and

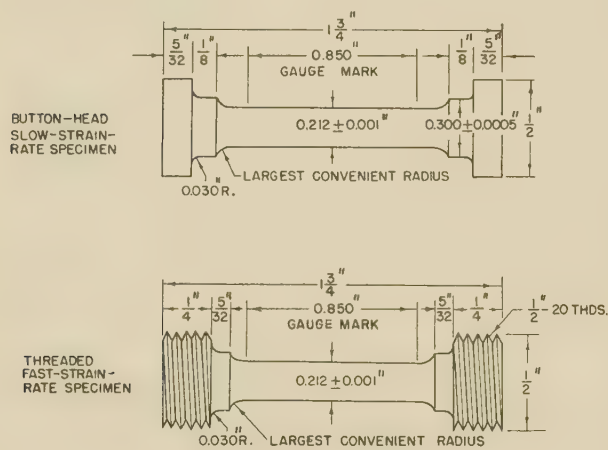


FIG. 1.—Test Specimens.

grain coarsening was accomplished by cold swaging the rods 5% † and annealing for 3½ hr. at 600° F. (315° C.). The swaged and heat-treated specimens were machined directly to the final shape.

All tests at the two low strain rates (0.05 and 10 in./min. movement of the test-machine head) were conducted on a hydraulic-type tensile machine with the aid of a special loading device designed to give an eccentricity (distance between loading and specimen axis) of <0.001 in.<sup>6</sup> Tests at 100 in./min. were made by adapting a hydraulic-type drawbench to tensile straining, and tests at 19,000 in./min. were conducted on a specially adapted drop-hammer. The eccentricity developed during testing at the two high strain rates was probably considerably in excess of that developed at the slow strain rates.

The testing temperature for the two low strain rates was obtained by placing a refrigerator or furnace around the specimen, the temperature being controlled by means of a thermocouple attached to the specimen. For testing at the two high strain rates, the test specimen and adapters were cooled, or heated, in an auxiliary unit. After the specimen and adapters reached the proper temperature, they were placed in the testing equipment and strained so that the time interval between removal from the auxiliary unit and the actual straining was approximately 4 sec.

\* All specimens were coated with Sauereisen cement and annealed in an air furnace, with the exception of a few specimens which were vacuum-annealed. No difference in properties could

Ductility values (contraction in area and elongation) were based on measurements of the specimen diameter and gauge-length with an optical comparator, before and after testing. Load/contraction-in-diameter curves were obtained by means of continuously recording test equipment to be described at a later date.

### III.—RESULTS AND DISCUSSION

#### 1. ENGINEERING TENSILE PROPERTIES

The tensile properties of the three binary alloys, as well as those of extruded pure magnesium which has been previously reported,<sup>7</sup> are shown as a function of the testing temperature with rate of straining as a parameter in Figs. 2–5. Since only the two low-strain-rate tests were conducted in a tensile machine, strength data (yield and tensile) could not be recorded for the high-strain-rate tests.

The slope of the tensile strength/testing-temperature curve obtained for each of the three binary alloys decreased abruptly at approximately the same temperature as that at which the ductility began its rapid increase with temperature. A behaviour similar to this in pure magnesium was shown to result from the fact that the metal recrystallized during straining, while a number of commercial magnesium (aluminum-bearing) alloys behaved similarly, accompanied by the precipitation of a second phase. An examination of the microstructure of the fractured test specimens of the binary alloys indicated that neither of these phenomena could account for their behaviour.

For the three alloys studied, increasing the strain rate from 0.05 to 10 in./min. produced only minor changes in the yield strength.

The completely body-centred cubic structure (11% lithium) gave yield-strength values that were the least temperature-dependent, in disagreement with Bechtold's suggestion that the yield strength of body-centred cubic metals is extremely temperature-sensitive.<sup>8</sup>

The 4 and 6% lithium alloys showed a rather abrupt loss in contraction in area with decreasing temperature over the temperature range in which the strength properties are changing gradually, suggesting that these two alloys may be subject to a transition-temperature type of embrittlement. If these can be interpreted as transition temperatures, the strain-rate sensitivity of these two alloys (shifting of the maximum in the contraction-in-area/testing-temperature curves) is considerably less than that for body-centred cubic metals. This is in agreement with the behaviour previously reported for a series of hexagonal, aluminium-bearing magnesium alloys<sup>7</sup> and for hexagonal pure zinc.<sup>9</sup>

Each of the alloys exhibited a distinct minimum in its ductility/testing-temperature curve. The magnitude of this depression increased as the lithium content increased; and the temperature at which the minimum occurred moved to higher temperatures as the rate of straining was increased. As shown in Fig. 6, the reciprocal of the absolute temperature of the ductility minimum is linearly related to the logarithm of the strain rate, i.e. an Arrhenius plot. The slope of the curves yielded an "activation energy" of 19,700 cal./g.-mol.

be detected with these two treatments.

† Contraction in area.



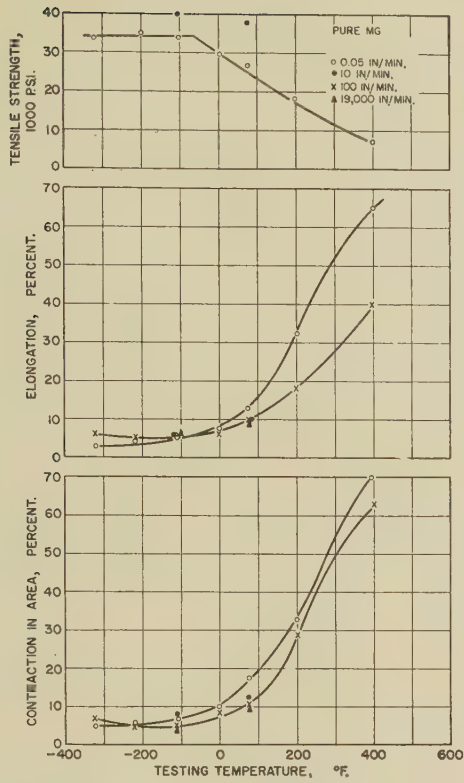


FIG. 2.—Pure Magnesium.

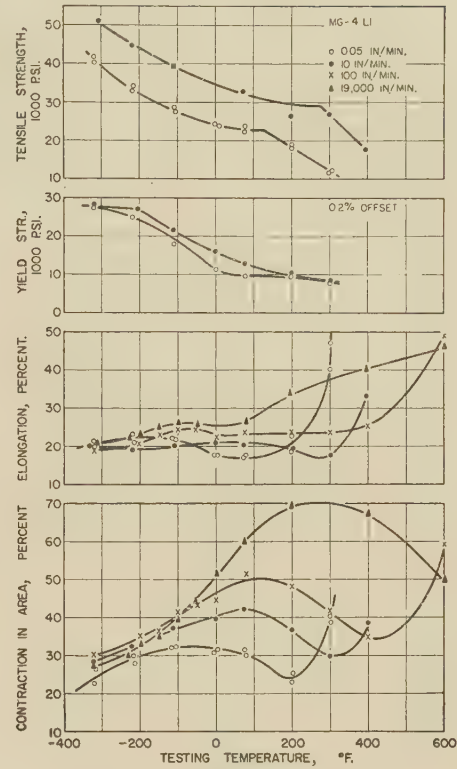


FIG. 3.—Magnesium-4% Lithium Alloy.

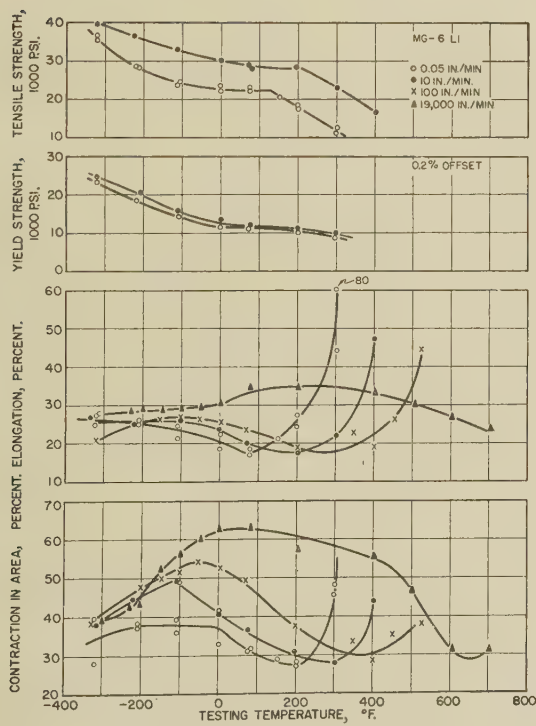


FIG. 4.—Magnesium-6% Lithium Alloy.

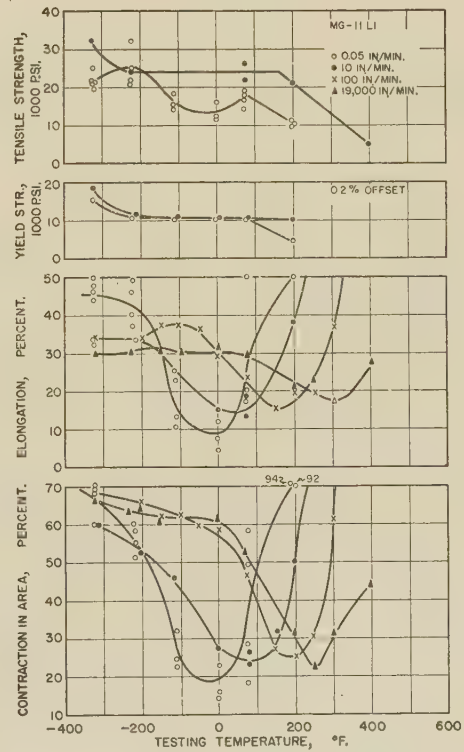


FIG. 5.—Magnesium-11% Lithium Alloy.

FIGS. 2-5.—Tensile Properties as a Function of Strain Rate and Testing Temperature.

The temperature at which the non-transition type of embrittlement occurs is more strain-rate sensitive than the low-temperature brittleness for the 4 and 6% lithium alloys (although both types of brittleness move to higher temperatures as the strain rate is increased). As a result, the embrittling-temperature ranges move apart, and the ductility between the two embrittling ranges increases as the strain rate increases.

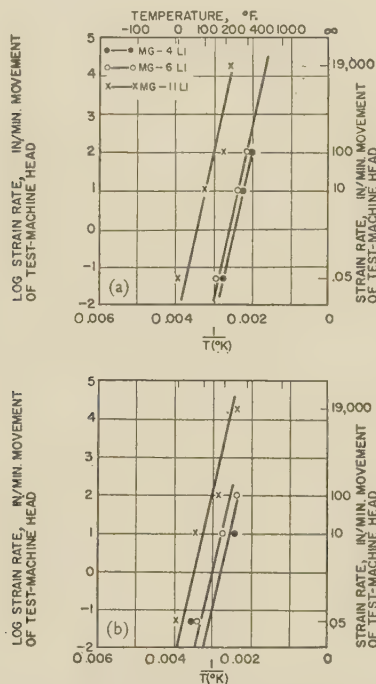


Fig. 6.—Arrhenius-Type Plot of the Ductility Minima Found in the Magnesium-Lithium Binary Alloys. Position of (a) the Contraction-in-Area Minima, (b) the Elongation Minima, with Varying Strain Rate and Temperature.

## 2. PLASTIC STRESS/STRAIN BEHAVIOUR

Stress/strain curves were obtained on specimens of each of the alloys over a range of testing temperatures at a slow strain rate, in the hope that these data would make possible a better understanding of the severe non-transition type of embrittlement found in these alloys. Moreover, since these alloys generally are excessively low in strength and high in ductility, a knowledge of the basic stress/strain relations might open up the possibility of developing a more useful combination of properties by cold working.

Because the investigation was concerned with the relative plastic behaviour of the alloys, these data are presented as load/contraction-in-diameter curves in Figs. 7-9. No allowance was made for the slight variation in initial specimen diameters, so that the loads are almost, but not absolutely, proportional to conventional stress. Further, since the diameter readings were obtained by means of a stationary radial gauge, the recorded strains are not necessarily the maximum strains developed at the bottom of the neck.

The load/contraction-in-diameter curves of the completely hexagonal structures—pure magnesium and the 4% lithium alloy—obtained at a slow strain rate and at

a variety of testing temperatures (Fig. 7) are quite normal in appearance in that they are smooth and the flow stress at any strain decreases with increasing testing temperature. The plastic-flow characteristics of the partially cubic (6% lithium) alloy (Fig. 8) and the completely cubic (11% lithium) alloy (Fig. 9) are quite complex. The 6% lithium alloy displayed a continuous decrease in flow stress with increasing testing temperature, excepting for temperatures between 0° F. (−18° C.) and room temperature. This alloy also developed serrated stress/strain curves at testing temperatures of 0° F. and room temperature. Testing at 0° F. produced serrations which were above an extrapolation of the smooth portion of the stress/strain curve, while at room temperature the serrations were below the extrapolation of the smooth portion of the stress/strain curve. The 11% lithium alloy showed a flow stress at any strain that was rather temperature-independent between −220° F. (−140° C.) and room temperature, much like its 0.2% offset yield strength (see Fig. 5). This alloy displayed the same type of serrations as the 6% lithium alloy; however, in the completely cubic material, the elevated type of serrations occurred at −220° F., while the depressed type occurred at 0° F.

It was not possible to determine how discontinuous yielding was affected by strain rate, because even strains of 10 in./min. were too fast to allow the recorder to define discontinuities in the stress/strain curve.

Since it requires appreciable plastic strains to develop the serrated stress/strain curves in these alloys, the discontinuous hardening found in the 6% lithium alloy at 0° F. and in the 11% lithium alloy at −220° F. appears to be strain-ageing. This is usually associated with precipitation from a supersaturated solid solution,<sup>10</sup> or with the locking of dislocations, as suggested by Cottrell.<sup>11</sup> The composition of the precipitate or cloud that might lock the dislocation is not known. Discontinuous softening of the alloys seems to be the result of some mechanism quite different from that which produces the discontinuous hardening.

Discontinuous yielding (hardening) in mild steels is found in the same temperature range as that at which steels are blue brittle, so that the precipitation that causes the serrations is thought to be the same as that which causes the embrittlement. While discontinuous yielding and the temperature-sensitive embrittlement in the magnesium-lithium alloys did not occur at the same temperature, it may be significant that in all cases discontinuous hardening occurs at a temperature just below that at which the ductility begins to be depressed.

Special attention was paid to the plastic behaviour of the magnesium-11% lithium alloy because previous attempts to harden multicomponent, cubic magnesium-lithium alloys by cold working were not successful.<sup>4</sup> This alloy, when slowly strained, had a high ductility at +200° F. (95° C.) (Fig. 5), so that it should be readily workable at this temperature. Any hardening developed by deforming at this elevated temperature should be retained at room temperature.

As shown in Fig. 9, stretching at +200° F. produced a load/contraction-in-diameter curve which had a negative slope after the diameter had been reduced about 0.001 in. A careful study of the specimen shape during straining indicated that the sample did not neck at this strain, at which the load went through a maximum, but remained



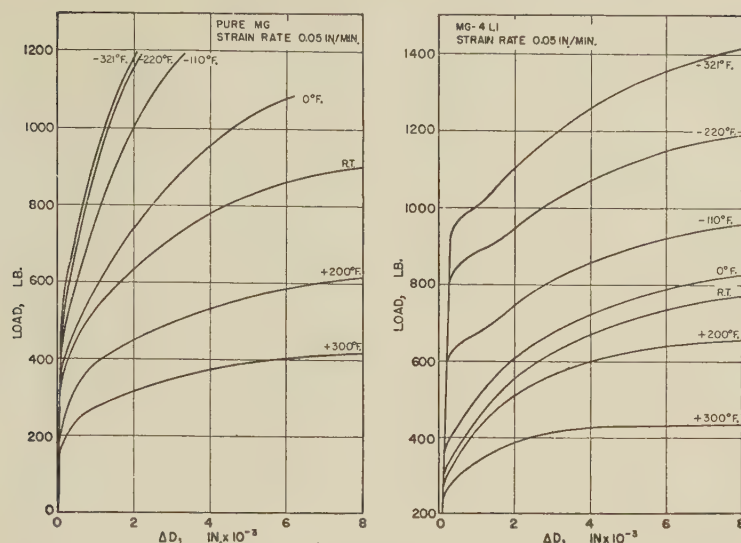


FIG. 7.—Load/Contraction-in-Diameter Curves for Pure Magnesium and Magnesium-4% Lithium Alloy Tested at Several Temperatures at a Slow Strain Rate.

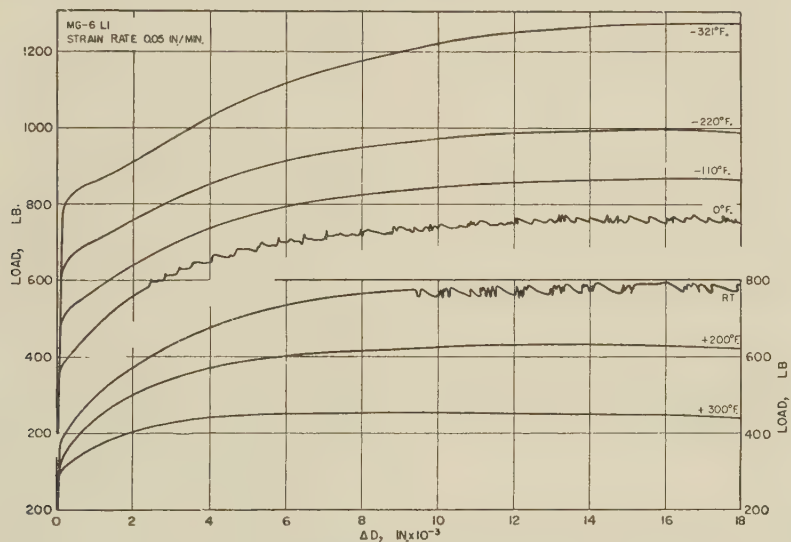


FIG. 8.—Load/Contraction-in-Diameter Curves for Magnesium-6% Lithium Alloy Tested at Several Temperatures at a Slow Strain Rate.

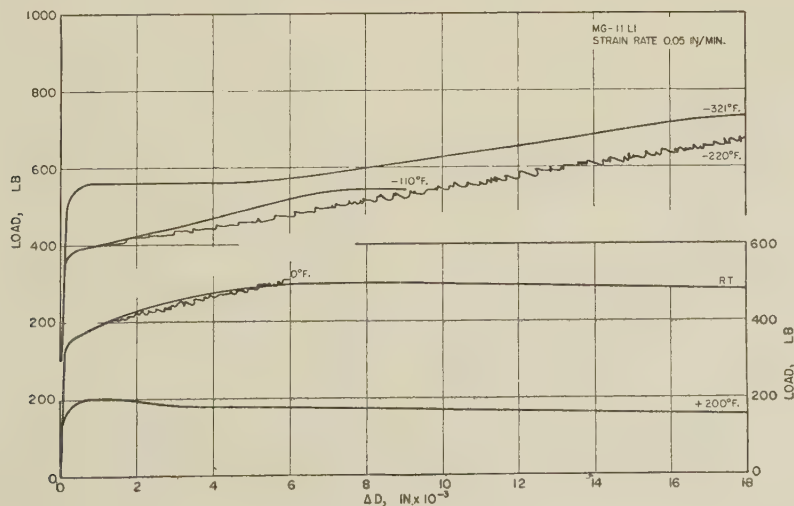


FIG. 9.—Load/Contraction-in-Diameter Curves for Magnesium-11% Lithium Alloy Tested at Several Temperatures at a Slow Strain Rate.

cylindrical until the diameter had contracted approximately 0.045 in. For the load to decrease during the test without forming a neck in the specimen requires the flow stress to be not only dependent on the strain, but be even more dependent on some other variable such as strain rate. A plot of true stress against natural strain yielded a negative strain-hardening exponent for natural strains between 0.01 and 0.10 (diameter contractions of 0.001 and 0.010 in.) and a slightly positive strain-hardening exponent above natural strains of 0.10. To confirm that these negative and small positive values for strain-hardening do not allow for hardening by working in the 11% lithium alloy, a few specimens were stretched various amounts at +200° F., after which their room-temperature hardness was determined. As shown in Fig.

transverse to the applied load. Within a single grain, the cracks were parallel to the twinning direction. Frequently, the cracks could be seen to be superimposed on a twin that had previously formed (Fig. 12 (a), Plate XXIV). Apparently the twinning and fracturing planes for this alloy are identical, or as Bruckner<sup>12</sup> suggests "cleavage may be initiated by the twin or the twin-deformed region".

The transgranular cracks when first detected were not a complete grain long, but generally of the order of half a grain long. The cracks were bow-shaped, suggesting that the void did not open instantaneously. Rather, it nucleated on a scale too small to be seen and then grew in length, widening to relax the stress about itself, and finally became wide enough for microscopic detection

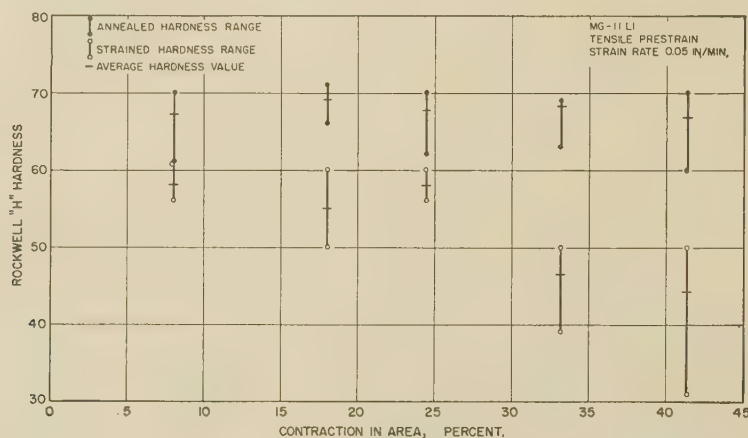


FIG. 10.—Loss in Room-Temperature Hardness as a Function of Percentage Strain for Magnesium-11% Lithium Alloy Strained at +200° F. (95° C.) at a Slow Strain Rate.

10, elevated-temperature straining produced room-temperature softening. This eliminates deformation as a hardening method for this alloy.

### 3. CRACK STUDIES OF STRAINED SPECIMENS

A previous study<sup>7</sup> of the microstructure of strained pure wrought magnesium and commercial aluminium-bearing magnesium alloys had shown that the poor ductility of the former was the result of a grain-boundary weakness that caused grain-boundary cracks to form after very small strains. Specimens of the alloys also developed premature cracks, but at higher strains, and in all cases these were transgranular.

Specimens of the three binary alloys were stretched by various amounts at different temperatures, after which they were longitudinally sectioned and examined microscopically, primarily in order to ascertain the cracking behaviour of each alloy. In all three of the alloys, microscopic cracks were found after straining to one-third to one-half of the fracture strain under the particular testing conditions. Specimens of the completely cubic alloy when strained at high and low temperatures were an exception to this, as described in a subsequent section.

#### (a) 4% Lithium Alloy

The cracks in the most dilute of the binary alloys were generally transgranular, and in a direction more or less

when the cracks were about half a grain long. The shape of the cracks also suggested that they initiated both at the edge of the grain and within the grain. Unless the orientation of adjacent grains was favourable, the cracks were unable to propagate from one grain to the next (Fig. 12 (b), Plate XXIV). The general fracturing mechanism appeared to consist of the initiation and propagation of a large number of cracks one grain long, while the metal was being strained. Only when the strain was close to the fracture ductility were the stresses acting on the uncracked grains sufficiently large for the small cracks to join by propagating through less favourably oriented grains.

Cracks formed in these alloys at all testing temperatures and strain rates were transgranular, with the possible exception of the specimens tested at the highest temperature (600° F.) (315° C.).

#### (b) 6% Lithium Alloy

The cracking behaviour of the 6% lithium alloy was identical with that of the 4% alloy in those regions of the specimen where only the hexagonal phase was present. In the same specimen, cracks appeared to be more readily initiated at the boundary between the two phases and were always more dense near the two-phase area than in those regions where the hexagonal phase only was present (Fig. 13 (a) and (b), Plate XXIV). Near



the two-phase structure, voids formed both inter- and transgranularly. As in the 4% alloy, cracking in the 6% lithium alloy was probably intergranular at 600° F.

#### (c) 11% Lithium Alloy

The cracking behaviour in the totally cubic alloy could be completely correlated with the ductility. This alloy always displayed intergranular voids at those strain rates and testing temperatures which yielded low values of ductility (Fig. 14, Plate XXV). These voids, like those in the other two alloys, were detected microscopically when they were about half a grain in length, at which instant the strains in the specimen were equal to one-third to one-half of the fracture ductility. At testing temperatures above and below that of the ductility minimum, microscopic cracks were not found, even at strains just less than the fracture strain. These ductile specimens appeared to be fracturing transgranularly.

The low ductility of this alloy on slow testing at room temperature is consistent with the room-temperature tensile behaviour of slowly strained cubic ternary alloys (containing either aluminum or zinc in addition to magnesium and lithium). Loonam<sup>13</sup> attributed the brittleness of the ternary alloys to their high sodium content. The very high sodium content of the 11% lithium alloy (see Table I) suggests that such might also be the case here. Busk, Leman, and Casey,<sup>5</sup> by analysis of etching solutions that had been in contact with intergranularly fractured and with sawn surfaces of magnesium-lithium alloys, suggested that sodium produced embrittlement by collecting at the grain boundaries. Since it was found in the present investigation that the cubic, 11% lithium alloy was ductile at high and at low temperatures and fractured transgranularly, it must be assumed that sodium had not collected in the grain boundaries of the specimens tested under these conditions. Hence, in the intergranularly cracked specimens, the sodium would have to diffuse to the grain boundaries during testing, suggesting that the activation energy of 19,700 cal./g.-mol. obtained from Fig. 6 is the activation energy for the diffusion of sodium in magnesium-lithium alloys. Unfortunately, an experimental measure of this quantity is not available, nor, as a matter of fact, would one expect to find this same activation energy for the hexagonal (4% lithium), or the mixed hexagonal and cubic alloys (6% lithium).

#### (d) Effect of Grain-Size

If intergranular cracking requires the sodium to diffuse to the grain boundaries, one might expect the position and magnitude of the ductility minima in Fig. 5 to be a function of the grain-size of the material. For this reason, both the tensile behaviour and microstructure of grain-refined and grain-coarsened specimens of the 11% lithium alloy were studied. Altering the grain-size produced very minor changes in the tensile properties (Fig. 15). The cracking behaviour of fine-grained and coarse-grained material was identical with that found in the specimens with the as-received grain size. This, of course, does not eliminate the possibility of diffusion of sodium to the grain boundaries as the cause of embrittlement, but does require the diffusion to be highly localized.

Intergranular cracking which leads to reduced ductility has been reported in pure magnesium<sup>7</sup> and

in a magnesium-0.2% lead-0.02% iron alloy.<sup>14</sup> Grain-boundary cracking in the pure magnesium encompassed large portions of the grain boundaries, and the cracks were smooth-sided. The magnesium-lead-iron alloy formed cavities around sub-grains which were in the neighbourhood of a major grain boundary, so that the voids were quite irregular. The intergranular cracks formed in the 11% lithium alloy were similar to those

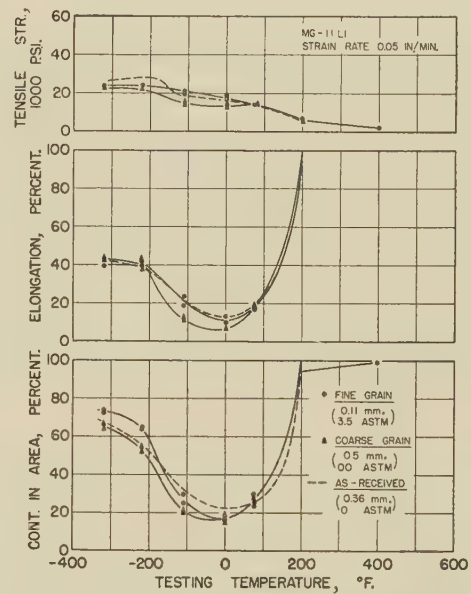


FIG. 15.—Comparison of Tensile Properties of Magnesium-11% Lithium Alloy Specimens Tested at a Slow Strain Rate as a Function of Grain-Size and Testing Temperature.

formed in pure magnesium in that they also were smooth-sided, indicating that it was the major grain boundaries which were the source of weakness.

## IV.—CONCLUSIONS

(1) Additions of lithium to magnesium generally improved its tensile ductility at sub-room temperature, while reducing the tensile strength. These property changes were continuous with increasing lithium content whether the structure was hexagonal (4% lithium), mixed hexagonal and cubic (6% lithium), or completely cubic (11% lithium), with the exception of a range of temperatures in which the cubic alloy suffered some embrittlement.

(2) Each of the three alloys displayed an embrittling temperature, which was strain-rate sensitive.

(3) The mixed hexagonal and cubic and the completely cubic alloy displayed discontinuous yielding of two different types. No evidence of discontinuous yielding was noted with the hexagonal structure. The completely cubic alloy also showed strain-softening at mildly elevated temperatures.

(4) The hexagonal and the mixed hexagonal and cubic alloys developed transgranular cracks that were detected microscopically at strains of one-third to one-half of their fracture ductility. These appeared to develop on twins.

(5) The completely cubic alloy showed premature intergranular cracks under testing conditions that yielded a low ductility. Cracks could not be found, even at strains close to the fracture strain, under testing conditions that produced a ductile behaviour. Since the sodium content of this alloy was rather high, the embrittlement could result from the localized diffusion of sodium to the grain boundaries.

#### ACKNOWLEDGEMENTS

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# SOLUTION-RATE STUDIES WITH LIQUID METALS: 1734

## SOLUTION OF COPPER IN LIQUID LEAD

### AND BISMUTH\*

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#### SYNOPSIS

A study has been made of the kinetics of the dissolution of solid copper in liquid lead and bismuth under nominally static and isothermal conditions, at temperatures in the range 360°–510° C. The dissolution followed an expression of the form  $n_t = n_0(1 - e^{-[KSt]/V})$ , where  $n_t$  = concentration of dissolved solute at time  $t$ ,  $n_0$  = saturation concentration,  $S$  = surface area of solid exposed to a liquid of volume  $V$ , and  $K$  = solution-rate constant. The solution-rate constant in the bismuth-copper system was about three times greater than that for lead-copper at any one temperature. The solution-rate constant varied with temperature thus:  $K = K_0 e^{-\Delta E/RT}$ , where  $\Delta E$  = the activation energy for the dissolution process.

The experimental data appear consistent with dissolution being a complex process involving diffusion of solute through a laminar boundary layer combined with convection effects introduced through density changes accompanying dissolution. From a general relationship between  $(n_t/n_0)$  and  $(t/t_0)$  it is possible to construct concentration/time relationships, knowing only the saturation concentration and the time to reach saturation.

#### I.—INTRODUCTION

THE kinetics of the dissolution of solid metals in liquid metals is one of the fundamental problems associated with liquid-metal technology.<sup>1</sup> Corrosion by liquid metals is usually of the solution type, as defined by Brasunas,<sup>2</sup> where mass transfer takes place from the hot to the cold limb owing to the differential of solubility of the solid metal in the liquid with respect to temperature. Here the rate of solution of the solid metal in the liquid may be the ultimate factor governing the rate of attack. In liquid-metal slurry systems, made up of an intermetallic compound dispersed in a liquid metal, growth of the solid particles may occur<sup>3</sup> if there is a finite solubility of the components of the solid in the liquid; the kinetics of this growth process is intimately associated with the rate of dissolution of the solid in the liquid metal.

In spite of its significance, little detailed work appears to have been carried out on the kinetics of the dissolution process. Limited information is available on the time required for a liquid-metal bath to reach saturation when in contact with a solid;<sup>4</sup> Epstein and Weber<sup>5,6</sup> indicate that the rate of dissolution of iron in liquid sodium is controlled by a surface reaction, while that of iron in liquid mercury is by diffusion in the liquid metal, but little experimental information is given for either system. Craighead, Cawthorne, and Jaffee<sup>7</sup> have made a detailed study of the solution rate of solid aluminium in molten aluminium-silicon alloy, in which they report effects due to temperature, agitation, and liquid- and solid-metal composition. This latter study is the most accurate existing work on dissolution; it was, however, carried out in relation to brazing operations, and the

results have not been analysed in such a way as to throw a great deal of light on the fundamental processes involved.

The present paper is a report of a study of the kinetics of the dissolution of solid copper in liquid lead and bismuth under static, isothermal conditions. These binary systems were selected for the following reasons. The dissolution is simple in the sense that the solid dissolves in the liquids with no intermediate compound formation, while the liquid metals do not dissolve appreciably in solid copper. The reported equilibrium solubilities<sup>8</sup> of copper in the two liquid metals are within the range 0.1–2.0 wt.-%, and therefore do not pose serious analytical problems. Furthermore, from studies of the wetting behaviour of copper by lead<sup>9</sup> and of the embrittlement of copper by bismuth,<sup>10</sup> some information is available on the relative magnitudes of the interfacial tensions in the two systems; this will be referred to when discussing possible mechanisms for the dissolution process.

#### II.—KINETICS OF DISSOLUTION

A theoretical basis for the kinetics of the dissolution of solids in liquids has been formulated from studies of the solution of inorganic and organic salts in water and non-aqueous solvents, and it is convenient to discuss the present results on this basis. The overall rate of dissolution is governed by the relative magnitudes of two separate rates, i.e. the rate at which atoms pass from the solid surface into the liquid layer immediately adjacent to the solid, and the rate at which atoms diffuse from this liquid layer into the bulk of the liquid bath. From this, the rate of dissolution may be formulated as outlined elsewhere.<sup>11</sup>

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The general expression thus derived for the rate of solution is:

$$n_t = n_0 [1 - e^{-k_s S(1 + k_s \delta/D)t/V}] \quad (1)$$

where  $n_t$  = solute concentration at time  $t$ ;

$n_0$  = saturation concentration at a fixed temperature;

$k_s$  = proportionality constant relating the rate of deposition of solute atoms to the concentration of solute atoms in the liquid;

$S$  = surface area of solid exposed;

$\delta$  = thickness of the laminar boundary layer;

$D$  = diffusion coefficient of the solute in the liquid;

$t$  = time from the start of dissolution;

$V$  = volume of liquid.

The experimental data may be analysed on the basis of the expression:

$$n_t = n_0 (1 - e^{-KSt/V}) \quad (2)$$

where  $K = D/\delta$  when diffusion in the laminar boundary layer is the slower step and therefore rate-controlling, and  $K = k_s$ , when the passage of solute atoms into the liquid is rate-controlling.

### III.—EXPERIMENTAL

#### 1. SELECTION OF METHOD

Initially, it was hoped to follow dissolution by the continuous measurement of a physical property which varied significantly with change in solute concentration. Surface tension, viscosity, and density measurements either did not have the necessary sensitivity or were experimentally complicated. Electrical resistivity, however, was relatively simple to measure and appeared to be the most suitable property, provided that the change with solute concentration was sufficiently marked. Preliminary tests indicated that, in fact, the changes in resistivity with the highest copper concentrations likely to be attained in the study were negligible and certainly well below the detection limits of the method of measurement. For these several reasons the method finally adopted had to be one based on chemical analysis of the liquid bath. Two alternative procedures were possible at this stage. In the first a large volume of liquid metal could be employed from which small samples might be withdrawn over the course of the dissolution; in the second a much smaller volume of liquid could be brought in contact with the solid and subsequently analysed for dissolved material. The latter was finally adopted because it was possible to take the entire liquid-metal volume in the final analysis, and thus no sampling error was likely to arise, as would have been the case with the first procedure; the adopted method had been successfully employed by Eldred<sup>12</sup> in an earlier study.

#### 2. MATERIALS, APPARATUS, AND PROCEDURE

The 5-mm.-dia. copper rod was of Johnson-Matthey spectrochemically pure metal, analysing 99.999% copper. Before test it was annealed for 1 hr. at 600°C. in a vacuum of  $10^{-5}$  mm. Hg and subsequently electro-

polished before introduction into the Hysil glass ampoule (see below).

Spectrochemically pure lead of 99.999% purity and pharmaceutical-grade bismuth were used; the latter contained the following impurities: Pb 44, Sn 27, Sb <10, Cd 0.6, Zn <1.0, As 1.0, Ag + Au 2, Co <0.5, Cu 3.0, Ni 1.0, Fe 16 p.p.m.

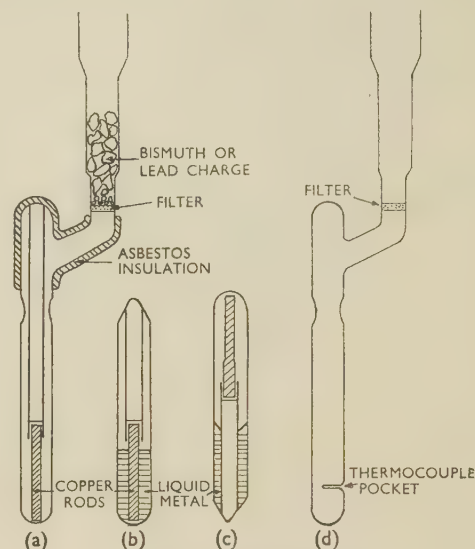


FIG. 1.—Stages in Production of Glass Ampoules.

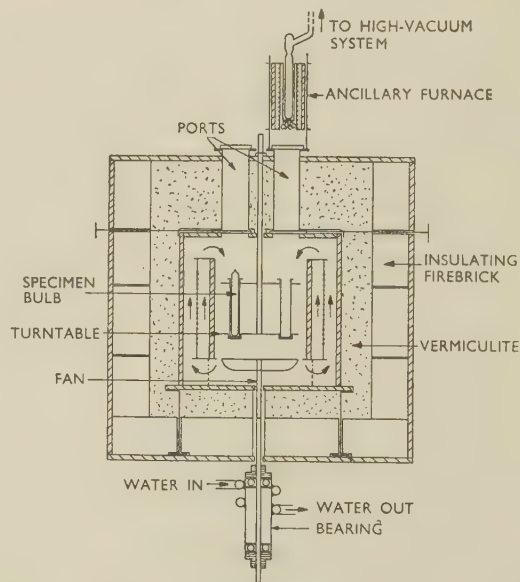


FIG. 2.—Air-Circulation Furnace (diagrammatic).

The individual tests were carried out in Hysil glass ampoules. The copper-rod specimens were placed vertically in the lower bulb of a unit which had an attached side-arm containing a sintered-glass filter disc, as shown in Fig. 1 (a); initially, the lead or bismuth, in solid rod form, was placed above this disc, which had a pore size of 100–120  $\mu$ . At the start of the test the composite ampoule was surrounded by an ancillary furnace unit, located on top of the main air-circulation furnace, while the open end of the ampoule was attached



to a high-vacuum system. The air-circulation furnace for the isothermal treatment of the glass ampoules is shown diagrammatically in Fig. 2. The inner furnace chambers were made of Sindanyo board, suitably insulated on all sides to give an isothermal region in the centre of the furnace; the Nimonic air-circulation fan rotated at approximately 1500 r.p.m. Tests showed that the maximum temperature differences were  $\pm 1^\circ$  at  $310^\circ\text{C.}$  and  $\pm 4^\circ$  at  $510^\circ\text{C.}$  Shuttered ports on the top of the furnace permitted the introduction and removal of the specimen bulbs, in a copper basket, the latter fitting into a stainless steel turntable capable of holding six specimens (Fig. 2). Temperature control was effected through a Temcon control system, located adjacent to the heating element; specimen temperatures were recorded by a Chromel/Alumel couple in the turntable.

After the composite ampoule had been assembled as described above (Fig. 1 (a)), the lower bulb, containing the electropolished copper rod, was outgassed under a vacuum of  $5 \times 10^{-5}$  mm. Hg at  $390^\circ\text{C.}$  for the lead-copper series, and  $290^\circ\text{C.}$  for the bismuth-copper tests. The lead or bismuth, placed above the filter disc, was melted and thoroughly outgassed under a similar vacuum, when a slight positive pressure of purified argon was sufficient to pass the liquid metal through the filter disc and down round the copper. The entire ampoule was re-evacuated to a pressure of  $3 \times 10^{-4}$  mm. Hg and the lower bulb sealed-off as shown in Fig. 1 (b). The specimen bulb and copper basket were quickly lowered, by attached handles, into the turntable of the air-circulation furnace, which was running at the chosen temperature; the time during which the copper and liquid metal were in contact during the sealing-off process was kept to 9–10 min. After a predetermined time, the specimen bulb was withdrawn from the air-circulation furnace and immediately inverted in order to separate the reactants (Fig. 1 (c)); the solidified metal was analysed for copper by standard analytical procedures. Individual specimens were treated for times ranging from  $\frac{1}{4}$  to 66 hr.

### 3. RESULTS

#### (a) Rates of Heating to Solution Temperatures

The specimen bulbs were held at temperatures of  $390^\circ$  and  $290^\circ\text{C.}$  for the lead-copper and bismuth-copper systems, respectively, during the sealing-off stages, and the times taken for the bulb temperatures to rise from these initial values to the preselected test temperatures were determined. These tests were carried out in a modified glass ampoule into which the liquid-metal charge was introduced normally, but which possessed a small thermocouple pocket to enable the rate of rise of temperature in the liquid bath to be measured (see Fig. 1 (d)). The time/temperature relationships for liquid lead and bismuth (Fig. 3), which rose respectively, from  $390^\circ$  to  $410^\circ$ ,  $460^\circ$ , and  $510^\circ\text{C.}$ , and from  $290^\circ$  to  $360^\circ$ ,  $410^\circ$ ,  $460^\circ$ , and  $510^\circ\text{C.}$ , show that the liquid-metal reaches the predetermined furnace temperature within 8 min. of being lowered into the turntable.

#### (b) Concentration/Time Relationships

The rates of solution of solid copper in liquid lead were determined at  $410^\circ$ ,  $460^\circ$ , and  $510^\circ\text{C.}$ , while

corresponding data for the solution of solid copper in liquid bismuth were determined at  $360^\circ$ ,  $410^\circ$ ,  $460^\circ$ , and  $510^\circ\text{C.}$  The concentration/time relationships, corrected as outlined below, are shown in Figs. 4 and 5 for the lead-copper and bismuth-copper systems, respectively.

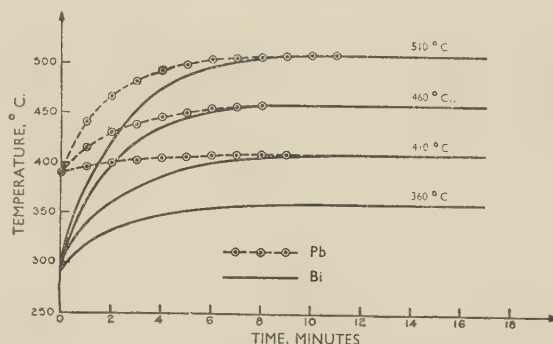


FIG. 3.—Heating Curves for Ampoules.

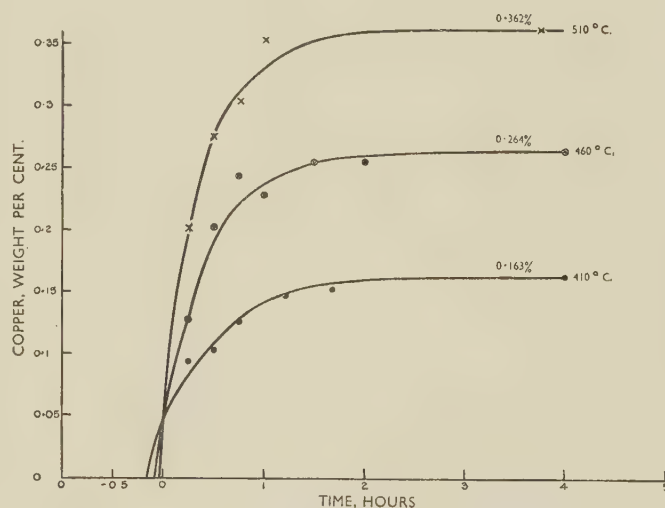


FIG. 4.—Corrected Concentration/Time Relationships for the Lead-Copper System.

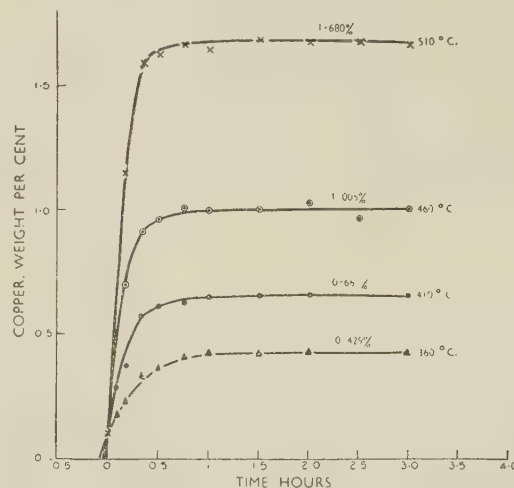


FIG. 5.—Corrected Concentration/Time Relationships for the Bismuth-Copper System.

## IV.—ANALYSIS OF DATA

The concentration/time relationships were analysed in terms of the general expression (see Section II):

$$n_t = n_0 (1 - e^{-Kst/V}) \quad (2)$$

Before this analysis was applied, the experimental relationships were corrected to allow for the copper introduced into the liquid bath during sealing-off, before

zero copper concentration; the intercept on the time axis gives a measure of the time-equivalent, at any temperature, of the sealing-off period. This time correction was applied to all the experimental data in determining  $t$  values for use in expression (2).

The data employed in evaluating expression (2) for the two systems at a number of temperatures are contained in Tables I and II for the lead-copper and bismuth-copper systems, and the plots of  $\log [n_0/(n_0 - n_t)]$  against  $t$  in Figs. 6 and 7. Solution-rate constants derived from

TABLE I.—Analytical Data for Lead-Copper System.

410° C. $n_0 = 0.163$ wt.-%				460° C. $n_0 = 0.264$ wt.-%				510° C. $n_0 = 0.362$ wt.-%			
Time, sec.*		$n_t$ , wt.-%	$\log \frac{n_0}{n_0 - n_t}$	Time, sec.*		$n_t$ , wt.-%	$\log \frac{n_0}{n_0 - n_t}$	Time, sec.*		$n_t$ , wt.-%	$\log \frac{n_0}{n_0 - n_t}$
M	C			M	C			M	C		
450	1050	0.066	0.2256	450	720	0.090	0.1783	450	540	0.141	0.2146
900	1500	0.082	0.3029	900	1170	0.127	0.2853	900	990	0.198	0.3439
1350	1950	0.096	0.3856	1350	1620	0.165	0.4264	1350	1440	0.241	0.4764
1800	2400	0.108	0.4711	1800	2070	0.192	0.5648	1800	1890	0.278	0.6350
2250	2850	0.119	0.5680	2250	2520	0.209	0.6812	2250	2340	0.298	0.7524
2700	3300	0.128	0.6675	2700	2970	0.222	0.7983	2700	2790	0.312	0.8600
3150	3750	0.135	0.7642	3150	3420	0.231	0.9032	3150	3240	0.322	0.9564
3600	4200	0.141	0.8689	3600	3870	0.237	0.9905	3600	3690	0.332	1.0813
4500	5100	0.150	1.0976	4500	4770	0.248	1.2178	4500	4590	0.346	1.3543
5400	6000	0.155	1.3083	5400	5670	0.255	1.4681	5400	5490	0.354	1.6551
6300	6900	0.158	1.5124	6300	6570	0.258	1.6435	6300	6390	0.358	1.9562
7200	7800	0.160	1.7336	7200	7470	0.260	1.8195	7200	7290	0.360	2.2577

\* M = Measured.

C = Corrected.

TABLE II.—Analytical Data for Bismuth-Copper System.

360° C. $n_0 = 0.429$ wt.-%				410° C. $n_0 = 0.661$ wt.-%				460° C. $n_0 = 1.005$ wt.-%				510° C. $n_0 = 1.680$ wt.-%			
Time, sec.*		$n_t$ , wt.-%	$\log \frac{n_0}{n_0 - n_t}$	Time, sec.*		$n_t$ , wt.-%	$\log \frac{n_0}{n_0 - n_t}$	Time, sec.*		$n_t$ , wt.-%	$\log \frac{n_0}{n_0 - n_t}$	Time, sec.*		$n_t$ , wt.-%	$\log \frac{n_0}{n_0 - n_t}$
M	C			M	C			M	C			M	C		
225	525	0.158	0.2009	225	405	0.249	0.2039	225	285	0.415	0.2309	225	255	0.485	0.1488
450	750	0.199	0.2718	450	630	0.355	0.3328	450	510	0.595	0.3896	450	480	0.880	0.3230
675	975	0.243	0.3651	675	855	0.441	0.4781	675	735	0.740	0.5805	675	705	1.280	0.6258
900	1200	0.274	0.4438	900	1080	0.513	0.6454	900	960	0.848	0.8041	900	930	1.465	0.8949
1125	1425	0.304	0.5384	1125	1305	0.560	0.8116	1125	1185	0.900	0.9800	1125	1155	1.564	1.1815
1350	1650	0.328	0.6325	1350	1530	0.587	0.9467	1350	1410	0.931	1.1348	1350	1380	1.613	1.4245
1575	1875	0.350	0.7360	1575	1755	0.601	1.0345	1575	1635	0.950	1.2400	1575	1605	1.637	1.6340
1800	2100	0.364	0.8251	1800	1980	0.614	1.1358	1800	1860	0.964	1.3781	1800	1830	1.649	1.7875
2250	2550	0.389	1.0422	2250	2430	0.636	1.4265	2250	2310	0.989	1.7760	2250	2280	1.662	2.0564
2700	3000	0.402	1.2125	2700	2880	0.648	1.6518	2700	2760	0.998	2.1348	2700	2730	1.671	2.6001
3150	3450	0.412	1.4343	3150	3330	0.652	1.8445								
3600	3900	0.421	1.7649												

\* M = Measured.

C = Corrected.

the specimens were lowered into the furnace. The sealing-off time was 9–10 min., so that the amount of copper introduced during this stage was fairly constant; analysis indicated this content to be 0.046 wt.-% for the lead-copper system and 0.10 wt.-% for the bismuth-copper system. On the basis of these figures for the copper contents of the respective liquid metals at zero measured time, the concentration/time relationships were drawn as shown in Figs. 4 and 5, and extrapolated to

Figs. 6 and 7 in conjunction with expression (2) are presented in Table III, and plots of  $\log K$  against  $1/T$  are shown in Fig. 8.

The concentration/time relationships were also analysed in terms of "reduced" quantities, where concentrations are expressed as fractions of the saturation concentration and times as fractions of the time required to reach saturation; the time to saturation was arbitrarily taken as that at which 98% of the saturation



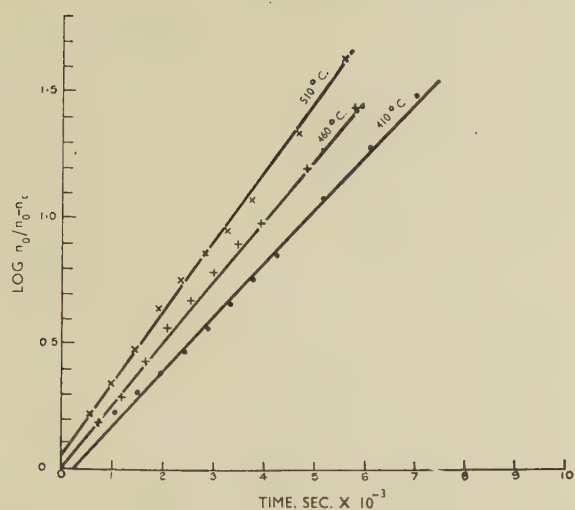


FIG. 6.— $\text{Log } \frac{n_0}{n_0 - n_t}$  / Time Relationships for the Lead-Copper System.

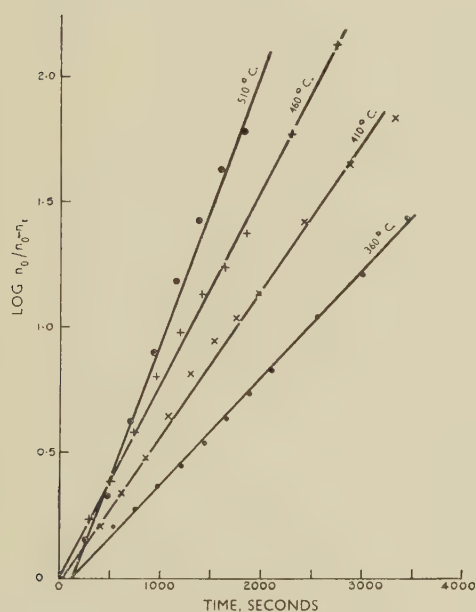


FIG. 7.— $\text{Log } \frac{n_0}{n_0 - n_t}$  / Time Relationships for the Bismuth-Copper System.

TABLE III.—Solution-Rate Constants for Lead-Copper and Bismuth-Copper Systems.

Temperature ° C.	° K.	Gradient of $\log \frac{n_0}{n_0 - n_t} / t$ Relationship	Ratio of Volume to Surface Area (V/S)	K
<i>Lead-Copper System</i>				
410	683	0.000225	0.838	$4.35 \times 10^{-4}$
460	733	0.000254	0.843	$4.93 \times 10^{-4}$
510	783	0.000311	0.849	$6.07 \times 10^{-4}$
<i>Bismuth-Copper System</i>				
360	633	0.00041	0.763	$7.2 \times 10^{-4}$
410	683	0.00058	0.770	$10.28 \times 10^{-4}$
460	733	0.00077	0.774	$13.7 \times 10^{-4}$
510	783	0.001065	0.779	$19.1 \times 10^{-4}$

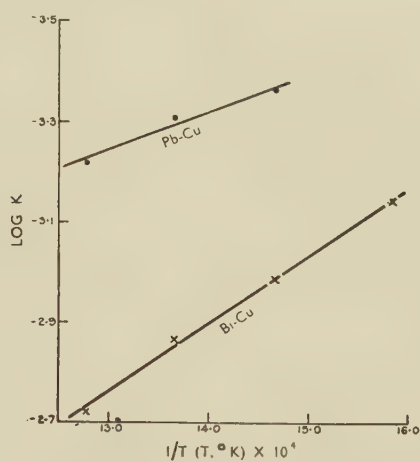


FIG. 8.— $\text{Log } K / (1/T)$  Relationships for the Lead-Copper and Bismuth-Copper Systems.

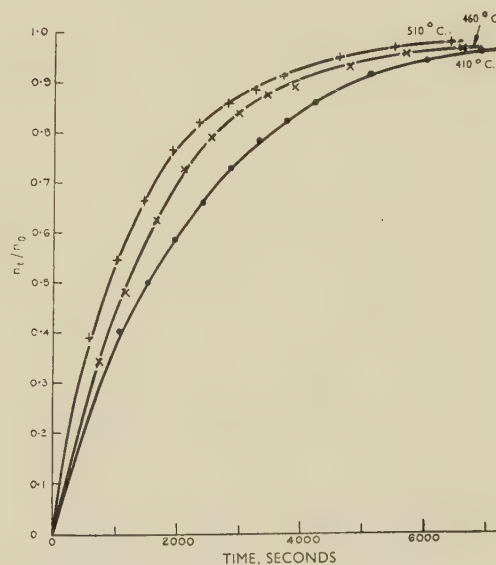


FIG. 9.— $(n_t/n_0)$  / Time Relationships for the Lead-Copper System.

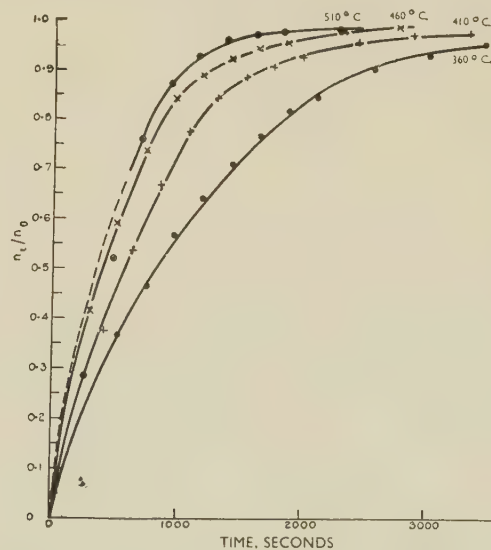


FIG. 10.— $(n_t/n_0)$  / Time Relationships for the Bismuth-Copper System.

concentration was attained. Two separate methods of plotting the reduced data were employed; in the one reduced concentrations were expressed as a function of time (Figs. 9 and 10 for lead-copper and bismuth-copper), while in the other reduced concentrations were related to reduced times (Figs. 11 and 12 for lead-copper and bismuth-copper).

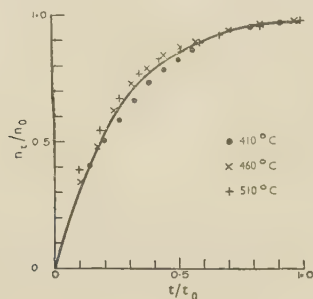


FIG. 11.— $(n_t/n_0)/(t/t_0)$  Relationships for the Lead-Copper System.

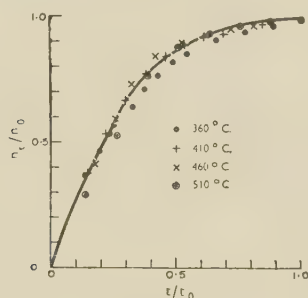


FIG. 12.— $(n_t/n_0)/(t/t_0)$  Relationships for the Bismuth-Copper System.

TABLE IV.—Solubility/Temperature Data for Lead-Copper and Bismuth-Copper Systems.

°C.	Temperature		Equilibrium Solubility	
	°K.	$1/T$ (°K.)	Wt.-%	At.-%
<i>Lead-Copper System</i>				
410	683	$14.65 \times 10^{-4}$	0.163	0.528
460	733	$13.65 \times 10^{-4}$	0.264	0.856
510	783	$12.78 \times 10^{-4}$	0.362	1.168
<i>Bismuth-Copper System</i>				
360	633	$15.82 \times 10^{-4}$	0.429	1.392
410	683	$14.65 \times 10^{-4}$	0.661	2.140
460	733	$13.65 \times 10^{-4}$	1.005	3.234
510	783	$12.78 \times 10^{-4}$	1.680	5.355

The saturation solubility/temperature data for the two systems are presented in Table IV; the heats of solution calculated from these data are 8.45 kg.-cal./mole for the dissolution of copper in liquid lead, and 8.85 kg.-cal./mole for that of copper in liquid bismuth.

## V.—DISCUSSION OF RESULTS

The conditions of the test are nominally static and isothermal, but convection effects may be introduced in the course of dissolution as a consequence of density

changes and heat generation in the liquid layers immediately adjacent to the solid. Furthermore, since the saturation concentrations are considerably higher in the bismuth-copper system than in the lead-copper system, the extent of such convection effects may be different in the two cases. The inherent nature of these convection effects makes their elimination difficult, and although they might be minimized by use of some form of solid capillary system, this would introduce other experimental complications. The possible influence of convection must be borne in mind in the following discussion.

The concentration/time relationships (Figs. 4 and 5) indicate that the liquid metal becomes saturated in a comparatively short time at any given temperature, viz. in approximately 2 hr. for the lead-copper system and 1 hr. for the bismuth-copper series. The initial rate of solution, at zero time and zero copper content, shows the comparatively strong effect of temperature. This rate has the following values in g./cm.<sup>2</sup> of solid surface/min., viz. lead-copper:  $1.98 \times 10^{-4}$  at 410° C.,  $6.74 \times 10^{-4}$  at 460° C.,  $12.09 \times 10^{-4}$  at 510° C.; bismuth-copper:  $1.17 \times 10^{-3}$  at 360° C.,  $2.66 \times 10^{-3}$  at 410° C.,  $7.04 \times 10^{-3}$  at 460° C., and  $11.16 \times 10^{-3}$  at 510° C.

This initial rate appears to be proportional to the saturation concentration at the temperature in question, in accordance with the analysis discussed below; it is ten times greater in the bismuth-copper system than in the lead-copper system at any given temperature.

The analysis of the experimental data in terms of expression (2) suggests that the rate of solution of solid copper in the two liquid metals is proportional to the difference between the saturation concentration and the actual concentration at any stage of the dissolution. Solution-rate constants for the two systems at a number of temperatures are presented in Table III, and it is convenient to discuss these in relation to the rate-controlling step in the dissolution.

If the rate-controlling step were in fact the rate of passage of solute atoms into the liquid, then  $K$  is related to  $k_s$ . Now  $k_s$  is equal to  $\bar{v}n_s/n_0$  and thus inversely proportional to the saturation concentration  $n_0$ , since  $\bar{v}$ , a frequency factor, and  $n_s$ , the number of solid atoms per unit area of copper surface, are constant. Thus, on this basis the solution-rate constant should not only decrease with temperature for any one system, but it should also be lower for the bismuth-copper series, since the saturation concentrations are higher than for the lead-copper system. Both facts are contrary to observation. Further, the variation of the solution-rate constant with temperature is of the form (see Fig. 8):

$$K = K_0 e^{-\Delta E/RT} \quad (3)$$

where  $\Delta E$  can be taken as the overall activation energy for the dissolution process; values of  $\Delta E$ , calculated from Fig. 8, were 3500 and 6400 cal./mole for the lead-copper and bismuth-copper systems, respectively. Now, if a chemical step at the solid/liquid interface were rate-controlling, the experimental activation energies for dissolution would be expected to vary in a manner corresponding to the relative values of the solid/liquid interfacial tensions. This follows if the activation energy for dissolution is regarded as a measure of the energy barrier to a copper atom passing from the bulk



of the solid through the interface into the liquid, and if the solid/liquid interfacial tension is assumed to be a measure of this energy barrier. Thus, the interfacial tension for the copper/liquid lead interface is well established<sup>9</sup> at 360 ergs/cm.<sup>2</sup> or 3300 cal./mole, while Morgan<sup>10</sup> has measured the copper/liquid bismuth tension as 280 ergs/cm.<sup>2</sup> or 2500 cal./mole. These interfacial-tension values are in the wrong order relative to the observed activation energies for dissolution in the two systems.

If the process is controlled by diffusion through the liquid, then  $K$  is related to  $D/\delta$ , where  $D$  is the coefficient of diffusion of the solute in the liquid and  $\delta$  is a thickness of liquid metal through which diffusion is taking place. If  $\delta$  is constant for one system at different temperatures,  $K$  is directly proportional to  $D$ , and the activation energies for dissolution should be similar to that for diffusion of the solute in the liquid metal. Experimental diffusion data are lacking for the two systems in question, but an order of magnitude for the activation energy can be obtained from the Stokes-Einstein equation. From the published data for the viscosity of the two liquid metals,<sup>13</sup> the activation energies for the diffusion of copper in liquid lead and bismuth were calculated as 3950 and 3300 cal./mole, respectively, compared with the corresponding energies for solution of 3500 and 6300 cal./mole. Thus the agreement is reasonable for the lead-copper system but poor in the other case, and the comparison of these energies is indecisive in determining diffusion to be the rate-controlling process. Recent studies both of diffusion<sup>14</sup> and of viscosity<sup>15</sup> in alloy systems have indicated that the activation energies for the two processes are strongly concentration-dependent, and it might be argued that a higher activation energy could be anticipated in the bismuth-copper system owing to the higher solute concentrations involved. However, there are no grounds for such a hypothesis, and the verification of this point must await experimental determination of the quantities involved.

The discussion so far has assumed that  $\delta$  remains constant in any one system at different temperatures. Values of  $\delta$  were calculated from the relationship  $K = D/\delta$ , using  $D$  values of the order of magnitude given by the Stokes-Einstein equation. For the lead-copper system  $\delta$  had values of  $2.0 \times 10^{-2}$ ,  $2.1 \times 10^{-2}$ , and  $2.0 \times 10^{-2}$  cm. at 410°, 460°, and 510° C., while for the bismuth-copper system the values were  $1.7 \times 10^{-2}$ ,  $1.4 \times 10^{-2}$ ,  $1.2 \times 10^{-2}$ , and  $1.0 \times 10^{-2}$  cm. at 360°, 410°, 460°, and 510° C. The values are reasonably constant for the lead-copper system at all three temperatures; but for the bismuth-copper system, though of the same order, they decrease consistently with temperature. The equilibrium solubilities at the corresponding temperatures are 0.163, 0.264, and 0.362% for copper in lead, and 0.429, 0.661, 1.005, and 1.680% for copper in bismuth, at the appropriate temperatures detailed above. Thus, the increase in solubility per 100° C. rise in temperature is approximately 0.2% for the lead-copper system and 0.6-0.8% for the bismuth-copper system. If convection, due to density variations in the liquid bath, is complicating the dissolution process, then these effects would be much more pronounced in the bismuth-copper system owing to the larger concentrations involved at any one temperature and to the greater increase in copper concentration with temperature rise.

To summarize, the experimental data are inconsistent with a surface step being rate-controlling in the dissolution process, but appear to be reasonably consistent with dissolution as a combined process of diffusion through a laminar boundary layer and convection as a result of density variations in the liquid bath. On this basis the similar magnitudes of the activation energies for diffusion and dissolution in the lead-copper system can be explained; the higher solution-rate constants and activation energy for dissolution in bismuth-copper are due to stronger convection effects consequent on the higher copper concentrations involved.

A natural consequence of expression (2) is that solution-rate constants can be extrapolated for both systems at temperatures other than those studied. From these extrapolated rate constants, it is easy to construct the appropriate concentration/time relationships.

The plots of reduced concentration ( $n_t/n_0$ ) against time (Figs. 9 and 10) follow an exponential relationship, as would be expected from expression (2); they likewise demonstrate the relatively faster dissolution in the bismuth-copper system relative to that in the lead-copper case. The relationships between the reduced concentrations ( $n_t/n_0$ ) and the reduced times ( $t/t_0$ ) (Figs. 11 and 12) are much more interesting. Not only are these relationships essentially identical for any one system at a number of temperatures, but they are identical for the two systems within the range of experimental error. The value of such a general correlation is that from a knowledge of the equilibrium concentration of any component in a liquid metal and of the time required to reach saturation, it will be possible to obtain a fairly precise concentration/time relationship for the system in question. The similarity of the relationships for the two systems studied suggests that the dissolution process is essentially similar in each case.

The saturation/temperature data now obtained for the lead-copper system (Table IV) can be compared with similar data determined elsewhere.<sup>16</sup> At the three temperatures employed the previously reported solubilities are 0.50, 0.88, and 1.38 at.-% copper, compared with the corresponding values from the present study of 0.53, 0.86, and 1.17 at.-%, respectively. The reported heat of solution is given as approximately 9700 cal./mole, compared with the present value of 8450 cal./mole. In both respects the agreement appears to be satisfactory.

## VI.—CONCLUSIONS

The rates of solution of solid copper in liquid lead and bismuth have been found to obey an equation of the form  $n_t = n_0 (1 - e^{-[KS]/V})$ , where  $n_t$  = concentration of solute in the liquid at time  $t$ ,  $n_0$  = saturation concentration of solute,  $S$  = surface area of solid exposed to the liquid whose volume is  $V$ , and  $K$  = solution-rate constant. The solution-rate constant in the bismuth-copper system is two and a half to three times that in lead-copper at any one temperature. Temperature alters the solution-rate constant according to a relationship of the form  $K = K_0 e^{-\Delta E/RT}$ , where  $\Delta E$  can be regarded as an activation energy for the dissolution process. The activation energies for dissolution have values of 3500 cal./mole for the lead-copper system

and 6300 cal./mole for bismuth-copper. From the temperature-dependence of the solution-rate constant it is possible to extrapolate concentration/time relationships for temperatures other than those studied.

The experimental data appear to be consistent with dissolution being a complex process involving diffusion of solute material through a laminar boundary layer and convection effects in the liquid due to density variations accompanying dissolution. On this basis the higher solution-rate constants for the bismuth-copper system result from stronger convection effects arising from the larger copper concentrations involved. Furthermore, the experimental data are inconsistent with a surface-transfer step being rate-determining under the experimental conditions employed.

The relationship between the reduced concentration and the reduced time is of a similar form for any one system at a number of temperatures and also for both systems studied. Thus, concentration/time relationships can be established knowing only the time to reach saturation and the saturation concentration. The comparable nature of this relationship for both systems indicates that the dissolution process is similar in the two cases.

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# EFFECTS OF CYCLIC STRESS AND FREQUENCY ON DEFORMATION MARKINGS IN FATIGUED COPPER \*

1735

By D. S. KEMSLEY,† M.Sc., F.M.T.C.

## SYNOPSIS

Fatigue deformation markings (striations) produced by cyclic stressing may be revealed both on the surface and in the interior of copper specimens by suitable etching. Fractured rotating-cantilever specimens tested at stresses ranging from  $\pm 10,000$  to  $\pm 25,000$  lb./in.<sup>2</sup>, and frequencies of 21 and 6000 c./m., were sectioned and examined by optical and electron microscopy after polishing and etching.

Striations were most numerous and distinct at low stresses and low frequency, and under these conditions they occurred in practically all crystals. At high stresses and high frequency, striations were much less numerous and definite, appearing in only an estimated one crystal in 500. Evidence is given that the striations are in fact slip traces, whose characteristics change from slip packets of approximately 1000 Å. interlamellar spacing at low stress to substantially single lines at high stress. Hardness results suggest that striations are not regions of intense localized work-hardening. The persistent slip bands obtained by Wadsworth and Thompson, when present, appeared to be associated with striations.

An explanation of the main observations is given in terms of interaction between dislocations. It is concluded that localized deformation most truly characteristic of cyclic stressing occurs only in low-stress, long-life specimens, and that as the stress increases deformation becomes less localized and exhibits similar features to those produced by unidirectional stress.

## I.—INTRODUCTION

SLIP bands formed on the surface of various metals fractured by cyclic stressing have been shown to be composed of several slip lines grouped together.<sup>1-4</sup> However, the general roughness of such surfaces makes them far from ideal for intensive microscopic examination, and this prompted an attempt to reveal deformation markings, both on the surface and in the interior of fatigue specimens, by etching. Copper was chosen as the test material, and the etching technique used was one recently found to reveal deformation markings in copper strained unidirectionally.<sup>5,6</sup> A phase of this work described previously<sup>7</sup> has indicated that deformation markings, or striations, were developed in low-stress copper fatigue specimens irrespective of the type of fatigue stressing imposed; they were not formed during initial application of the cyclic stress, and were not produced by the sectioning technique.

The investigation described in the present paper is concerned principally with the variation in the number and intensity of striations with cyclic stress and cyclic frequency. Such experiments might be expected to provide a clearer insight into the deformation processes under fatigue conditions. At the same time, evidence concerning the nature of the striations and their mode of formation was sought, and previous indications<sup>8</sup> of a relationship between striations and the "persistent slip bands" of Thompson *et al.*<sup>9,10</sup> were extended. The only previous work of a similar nature appears to be that of Forsyth,<sup>3</sup> who observed striations in an aluminium-0.5% silver alloy fatigued at low stress.

## II.—EXPERIMENTAL CONDITIONS

### 1. SPECIMEN PREPARATION

The material used was the same low-oxygen copper (99.95%) as that employed in previous experiments.<sup>7,8,11</sup> Eleven un-notched rotating-cantilever specimens<sup>12</sup> were machined to a fine finish from bars 5 in. long  $\times$  0.5 in. in dia., by turning out the centre portion to a minimum dia. of 0.350 in. on a 4-in.-radius contour (see Fig. 1). Two

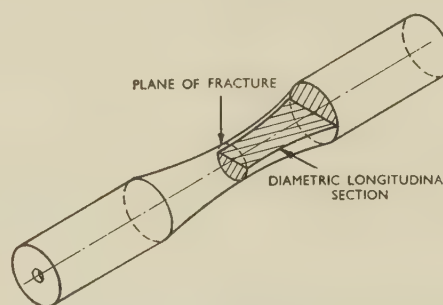


FIG. 1.—Illustrating Relation of Diametric Longitudinal Section to Fractured Specimen.

direct-stress specimens were also finely machined from rods 5 in. long  $\times$  0.625 in. in dia. to a minimum dia. of 0.357 in. on a 4-in.-radius contour. Six of the rotating-cantilever specimens and one direct-stress specimen were polished mechanically, and then electrolytically polished in orthophosphoric acid solution. Finally all specimens were vacuum-annealed at 600° C. for 1 hr.

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## 2. FATIGUE-TEST CONDITIONS

Variation in striation intensity was observed on specimens tested under the conditions given in Table I. Specimens subjected to stress amplitudes in the region of  $\pm 11,000$  and of  $\pm 20,000$  lb./in.<sup>2</sup> will subsequently be referred to as "low-stress" and "high-stress" specimens, respectively. The number of cycles to reach full

TABLE I.—*Fatigue-Test Conditions.*

Type of Stress	Specimen No.	Stress Amplitude, $\pm$ lb./in. <sup>2</sup>	Frequency, c./m.	Life to Fracture, cycles
Rotating cantilever	1	14,000	21	833,350
	2	16,000		201,700
	3	20,000		27,530
	4 *	11,000	6000	31,294,000
	5	14,000		1,978,000
	6 *	15,000		1,466,000
	7	16,000		687,000
	8 *	20,000		145,000
	9 *	25,000		35,800
Push-pull	10 *	9,000	2000	1,820,000
	11	16,000		218,000
Rotating cantilever	12 *	10,000	6000	3,800,000 †
	13 *	25,000		3,600 †

\* Electrolytically polished in orthophosphoric acid solution and annealed. No further surface preparation was necessary before testing, as the vacuum present during annealing was sufficient to retain the highly polished surfaces.

† Unbroken; this figure is 10% of the life to fracture at this stress level.

load varied with the fatigue-test conditions and was approximately 2500 cycles and 3500 cycles at low and high stress respectively, in the 6000-c./m. rotating-cantilever test. In the 21-c./m. tests, the full load was reached in approximately 30 cycles, while in the direct-stress tests, the corresponding figure was 2000 cycles. The lives given in Table I are the numbers of cycles from the full application of load to complete failure of the specimens.

## 3. EXAMINATION OF SPECIMENS

Specimens 1–11 were completely fractured, and of the two portions of each specimen thus available for examination, one was copper-plated and sectioned longitudinally, by a slitting wheel flooded with coolant, to provide a diametric longitudinal section, as illustrated in Fig. 1. This section was polished mechanically and then electrolytically in orthophosphoric acid solution, and examined by optical and electron microscopy. Macro- and micro-hardness tests were also carried out. The second portions of specimens 4, 6, 8, and 9 were examined by the optical microscope on the original curved surface in both the as-fractured state and after a subsequent re-electropolish and etch. Specimens 12 (low-stress) and 13 (high-stress), tested to only 10% of the total estimated lives, were similarly examined on the original curved surface.

Since the nominal applied stress on a rotating-cantilever specimen acts only on the surface, the actual stress at any point below the surface is less, and has a value of zero at the neutral axis. Hence, the true effect of the

nominal stress can be obtained only from observations and measurements made close to the outer surface of the specimen and as near as possible to the main fracture. This procedure was followed throughout.

## (a) Optical Micrography

Earlier work on the development of striations in the interior of low-stress copper fatigue specimens by etching<sup>7</sup> showed that a dilute acid ferric chloride solution produced the best results. This reagent consisted of: 5 g. ferric chloride, 10 ml. hydrochloric acid (conc.), and 100 ml. water. Certain precautions were necessary to give satisfactory results with it, viz. filtering before use to remove suspended matter, drying specimens with hot water rather than with alcohol, and cooling to room temperature before etching to avoid the deposition of microscopic crystals. A standard etching time of 4 sec. was adopted. No new markings were developed in any specimens by other etchants known to produce deformation markings in copper strained unidirectionally.<sup>5</sup>

Vertical illumination was used exclusively, since no additional information was obtained from examination by oblique, dark-field, or phase-contrast illumination, polarized light, or interferometry.

## (b) Hardness Tests

The macro-hardness of each fractured specimen was measured on the longitudinal section 1 mm. from the fracture and close to the original surface, using a standard Vickers machine with 2½ kg. load. In addition, certain micro-hardness tests were made with a dead-loading type of machine, the 3-g. load being applied for 15 sec. The indenter was a standard Vickers-type pyramidal diamond, so that macro- and micro-hardness results were comparable.

## (c) Electron Micrography

Replicas, which were methyl methacrylate (positive) and carbon (negative) shadowed with chromium, were prepared from an as-polished longitudinal section of specimen 2, and from similar sections of specimens 2, 3, 4, 6, 8, and 9, after etching for 1 sec. Replicas were examined with a standard R.C.A. electron microscope.

## (d) X-Ray Examination

Back-reflection X-ray-diffraction patterns (copper  $K\alpha$  radiation) were obtained from specimens 4, 6, 8, and 9, both before testing and after fracture. In the latter case, the X-ray beam impinged on the original surface approximately 1 mm. from the main crack.

## III.—METALLOGRAPHIC EXAMINATION AND RESULTS

## 1. OPTICAL-MICROSCOPIC EXAMINATION

As would be expected, the surfaces of the electro-polished specimens after fracturing contained many slip bands, more being present at high stress than at low stress, and in addition the surfaces of the high-stress specimens showed rumpling. In both low- and high-stress specimens, subsequent electropolishing to a depth of 4  $\mu$  removed all slip-band traces. Specimens were



then given the standard etch in acid ferric chloride solution, and striations were developed in low-stress specimens which corresponded well with the original surface slip markings (see Figs. 2 and 3, Plate XXVI). However, no striations were revealed in the high-stress specimens.

Examination was next extended to the interior by examining longitudinal sections (see Fig. 1). The influence of magnitude and frequency of stress on the development of striations is shown in Figs. 4-9 (Plate XXVI). These micrographs were taken on longitudinal sections at the main fracture in each specimen and approximately 0.1 mm. in from the edge of the specimen, i.e. from the original surface. A portion of the main crack is included in each case. Striation density is greatest at low stress ( $\pm 14,000$  lb./in.<sup>2</sup>) and decreases practically to zero at high stress ( $\pm 20,000$  lb./in.<sup>2</sup>). This variation was confirmed on longitudinal sections of push-pull specimens (see Figs. 10 and 11, Plate XXVII). Although striations were not detected in the high-stress rotating-cantilever specimens at low magnification (Figs. 6 and 9), they were visible at high magnification (Figs. 12-15 Plate XXVII). It was estimated that one in every two crystals contained striations in low-stress specimens, but only one in every 500 in high-stress specimens.

In addition to showing the effect of stress, Figs. 4-9 indicate clearly that frequency also influences the number of striations present, which is greater at low than at high frequency. This difference is more marked at low stresses.

In view of the clear difference in the number of striations observed in high-stress and low-stress specimens, these markings might be expected to occur in those regions across the sections of high-stress specimens where the stress was sufficiently low. However, no such areas were detected.

Since striations correspond closely with surface slip bands (see Figs. 2 and 3), they are presumably traces of  $\{111\}$  slip planes. Additional evidence obtained on this point was as follows. First, Fig. 10 (Plate XXVII) shows one crystal in which three families of striations are present. The angles between these sets are consistent with the view that striations are traces of  $\{111\}$  planes; in no way can the angles be arranged on a stereographic projection to correspond to traces of other planes. Secondly, striations are often found parallel to annealing-twin boundaries which have a  $\{111\}$  habit (see for example, Fig. 11, Plate XXVII, and 25, Plate XXVIII).

Other characteristics of striations have been observed. When striations meet grain boundaries, a "serrated" line often results (see Figs. 16 and 17, Plate XXVII). Localized concentrations of striations are sometimes visible at grain boundaries, and occasionally striations continue across a grain boundary (see Figs. 16 and 17). Kinks in annealing-twin boundaries associated with striations are shown in Fig. 18 (Plate XXVIII); the boundaries are concave at each end of a striation.

It has been reported<sup>9, 10</sup> that certain of the slip markings on copper fatigue specimens remain after electrolytic polishing, and evidence was sought of any relationship between such "persistent slip bands" and striations. Accordingly, a specimen (No. 12) was fatigued to approximately 10% of the life at low stress, and electrolytically polished (these being the conditions

under which "persistent slip bands" are known to develop<sup>8</sup>). Standard etching revealed that the "persistent slip bands" present appeared to be closely associated with striations (see Fig. 19, Plate XXVIII). Furthermore, examination of a high-stress specimen (No. 13) prepared in the same way showed neither "persistent slip bands" nor striations. In view of this difference, it is of interest that these two specimens differed neither in hardness (65 D.P.N.) nor in the characteristics of the slip bands present on the surface before polishing. Another feature was that "persistent slip bands" were frequently found along annealing-twin boundaries (Fig. 20, Plate XXVIII).

## 2. HARDNESS TESTS

The Vickers hardness values of all fractured specimens measured 1 mm. from the main crack lay between 66 and 75 D.P.N. irrespective of stress and frequency, in good agreement with results presented elsewhere.<sup>11</sup>

Local concentrations of striations near grain boundaries, similar to, but more extensive than, those shown in Fig. 16, were observed in ten crystals of a low-stress specimen (No. 4). Micro-hardness tests were carried out on each of these crystals in the region of striation concentration and also in the relatively striation-free body of the crystal. Average micro-hardnesses were 89 and 68 D.P.N., respectively (estimated accuracy  $\pm 6$  D.P.N.). It was not possible to measure the hardness of an individual striation with the apparatus available.

## 3. ELECTRON-MICROSCOPIC EXAMINATION

No striations were visible on an electropolished fractured low-stress specimen (No. 2), but they developed in all etched specimens. The variation in appearance with increasing stress (specimen Nos. 4, 6, 8, and 9) is shown in Figs. 21-24 (Plate XXVIII) at a magnification of 12,000. Striations produced at low stress are composed of groups of lines, each distant some 1000 Å. from its neighbour; as stress is increased, well-defined groups cease to exist, and are replaced by single lines. In addition, the number of crystals in which such effects are observed diminishes rapidly.

Striations were sometimes seen to continue across, and be diverted by, grain boundaries, as previously observed optically (see Fig. 16). In isolated cases where striations crossed one another, no deviation was apparent, even at high magnifications. Striations and annealing-twin boundaries were frequently parallel and contiguous (see Fig. 25, Plate XXVIII).

## 4. X-RAY-DIFFRACTION PATTERNS

All specimens before testing showed sharp X-ray-diffraction spots characteristic of completely annealed material. When specimens were examined after fracture, normal blurring of spots occurred in low-stress specimens and ultimately led to the formation of complete rings at testing stress.

## IV.—DISCUSSION

### 1. NATURE OF STRIATIONS

The striations produced by cyclic stressing are removed by polishing and revealed again by etching; this might indicate that they are mechanical twins. However, they

possess a fine structure (see Fig. 21, Plate XXVIII) and correspond quite closely with the original surface slip bands (cf. Figs. 2 and 3, Plate XXVI). In addition, unpublished results of annealing experiments on a fractured low-stress specimen have shown that the striations simply disappear over a fairly wide temperature range and that recrystallization does not occur. It thus seems quite definite that striations are traces of slip packets, rather than mechanical twins. This is in line with the conclusions of several investigators on copper deformed statically.<sup>5, 6, 13-15</sup> Furthermore, the fact that striations are present in specimens at 10% of the fatigue life rules out the possibility that they are formed at the instant of final fracture.

Several workers have found that slip bands produced on the surface of specimens during fatigue have a fine structure.<sup>1-4</sup> The present work confirms this, and also shows for the first time that similar characteristics can be revealed in the interior (Figs. 21-25, Plate XXVIII). The estimated interlamellar spacing of 1000 Å. in low-stress specimens is rather large compared to the 200 Å. measured by Forsyth<sup>4</sup> on surface slip bands in fatigued aluminium. The significance, if any, of this difference is not clear, since the measurements were made on different materials, and in the interior and on the surface, respectively. Further, in the present case, etching may have obliterated fine lines, or may not have revealed them at all.

The presence of a high concentration of striations does not seem to be associated with the same macroscopic hardness as is observed in a fractured tension specimen, i.e. 130 D.P.N. approximately. Hence, it appears unlikely that striations themselves are sites of intense localized work-hardening.

## 2. CONDITIONS FOR STRIATION FORMATION

Forsyth<sup>3</sup> has observed striations on the surface of a low-stress aluminium-0.5% silver fatigue specimen. A similar surface phenomenon has been found in the present work on fatigued copper by suitable etching, and although striations appeared in both high- and low-stress specimens, they were very much more prevalent in the low-stress specimens, particularly at low frequency. Furthermore, it has been possible to reveal similar features in the interior. The absence of striations in high-stress specimens in those regions where the stress would be low because of the stress distribution across the section, is at first sight rather surprising. The reason for this could be that the number of cycles involved in fracturing a high-stress specimen is insufficient to develop striations in the low-stress regions. This has been partially confirmed by cycling a specimen at low stress ( $\pm 11,000$  lb./in.<sup>2</sup>) for the number of cycles required to produce fracture at high stress (35,000 cycles at  $\pm 25,000$  lb./in.<sup>2</sup>), i.e. for 0.1% of the expected life at the low stress, when no striations were observed, although slip bands were already present on the surface.

The virtual absence of striations at high stresses may be attributed either to a different mode of deformation from that occurring at low stresses or to the continual formation and disruption of striations. This point has been elucidated by cycling a specimen at low stress until striations were well developed (25% of the estimated life), and then running to fracture at high stress. No

change in the striations present was produced by the high-stress treatment. Thus, there appears to be an essential difference between the modes of deformation under high and low cyclic stresses. This is borne out by electron-microscopic examination, which showed that the numerous striations present in low-stress specimens consisted of lines clustered into packets, while the very few present in high-stress specimens were essentially single lines. It is interesting to note that a copper specimen deformed in tension to the same hardness as a fractured fatigue specimen has a rumpled surface, exhibits continuous rings in the X-ray pattern, and shows no striations in the interior.<sup>7</sup> This would imply that the modes of deformation as revealed by etching are similar under high cyclic stress and unidirectional stress.

## 3. THEORY OF STRIATION FORMATION

Honeycombe<sup>16</sup> has pointed out that slip packets are developed during unidirectional stressing near the melting point and during creep stressing at lower temperatures. He has suggested that the production of slip packets during cyclic stressing at room temperature may be due to localized high temperatures on slip planes. However, this would imply that the number of striations should increase with stress and frequency, which is the reverse of the evidence presented here.

The only available theory of the formation of slip packets by cyclic stressing in terms of dislocations appears to be that of Louat.<sup>17</sup> For small strains, he has argued, following the observations of Brown on the formation of slip bands in aluminium,<sup>18</sup> that, as the stress is raised in the first half-cycle, single slip lines form at a distance apart which is characteristic of the metal concerned and which is smaller the greater the stress. In the process of this slip-line formation, dislocations emitted by a source develop jogs, some of which are multiple, as a result of successive interactions with other dislocations crossing the slip plane and having Burgers vectors with a component normal to the slip plane. Louat considers that the drag caused by these jogs on the essentially screw-type dislocations in which they form leads to the production of parallel lines of essentially edge-type dislocations of opposite sign. The mutual annihilation of these dislocations is considered to be difficult if the jogs are multiple or if the result of the annihilation is the production of interstitial atoms. In these circumstances, the parallel dislocations present obstacles around which further moving dislocations wrap themselves. It is envisaged, as a consequence of the stresses produced by this double pile-up around the original pair, that some dislocations will be pushed past their twins only to encounter further dislocations, and that some mutual annihilation does occur. The resultant vacancies or interstitial atoms are in part collected by dislocations in and around the centre of the pile-up ("core"), causing them to climb, and leading to an increasingly complex dislocation network.

Louat shows also, by considering the stresses produced by such double pile-ups, that there will be a tendency for slip to occur close to the original slip plane, which is greater at higher temperatures (see Brown<sup>18</sup>); this he suggests may be the explanation of the observed interlamellar spacing (200 Å. for aluminium). On the other hand, he finds that at greater distances from the original



slip plane, the stresses are such as to oppose the motion of dislocations and are inversely proportional to the distance from the slip plane. Concluding that there will be negligible dislocation motion during unloading and re-loading in the second half-cycle, he then suggests that the stresses which previously hindered slip now tend to assist this process, and that therefore the three most probable sites for slip in the second half-cycle are: (i) on the existing slip planes; (ii) a few Å. from them, but at distances much less than the characteristic interlamellar spacing; and (iii) at distances greater than the interlamellar spacing but much less than the distance between the single slip lines initially present. Which of these possibilities will occur is not clearly defined, but it might be expected that continued cycling would lead to increasing numbers of slip packets developing from single slip lines. Further, the number of slip lines in a group should depend on the number of cycles rather than on the magnitude of the applied stress.

From the above, it would appear that at low stresses involving many repetitions of stress to fracture, ample opportunity is provided for the formation of slip packets by the multiplication process envisaged by Louat. On the other hand, under high-stress conditions, and also of course in unidirectional stressing, any such features would be much less developed. Apparently, the etching technique adopted is capable of revealing slip packets only when these have grown to a considerable extent—much more than is necessary for the appearance of visible slip traces on the surface. This is confirmed by the inability of the etching reagent to reveal striations in a low-stress specimen cycled to only 0.1% of its life, when surface slip bands were already visible. Hence, at high stress a large number of slip packets exist at an early stage of development, while at low stress a relatively small number of highly-developed slip packets are present. This conclusion also explains the X-ray observations.

The theory of the mechanism of slip-line multiplication does not include specific reference to the frequency of stressing, although the number of striations actually observed is greater at low than at high frequency. If the tendency for slip-line multiplication is the same in both cases, it would appear that fewer lines multiply at high frequency because of the shorter time per cycle for which the nominal stress is applied. It may be, however, that the tendency for multiplication, which will

depend on the formation of "cores", is itself lower at high frequency. This may occur if vacancies generated by slip do not diffuse away from the slip planes to a significant extent when the time between successive cycles is relatively short.

## V.—CONCLUSION

It is suggested that for copper, localized deformation most truly characteristic of cyclic stress occurs predominantly in low-stress, long-life specimens, and that as the stress increases the deformation becomes less localized and more like that produced by unidirectional stress.

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# 1736 THE COLD-ROLLED TEXTURE OF HAFNIUM\*

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## SYNOPSIS

Arc-melted crystal-bar hafnium containing 3% zirconium was given 95% reduction in thickness by cold rolling to 0.004 in. strip. The preferred orientation of the strip was studied by a Geiger-counter-spectrometer X-ray-diffraction technique. The material showed a (0001) [10 $\bar{1}$ 0] texture rotated 25° toward the transverse direction about an axis in the rolling direction.

## I.—INTRODUCTION

PREVIOUS investigators<sup>1</sup> have noted the marked similarity in the cold-rolled textures of titanium, zirconium, and beryllium—all hexagonal metals with  $c/a$  ratios near to, but less than, 1.63. The predominant structure reported is a preferred orientation in which the [10 $\bar{1}$ 0] direction is parallel to the rolling direction and the basal (0001) plane is tilted in the transverse direction at various angles, depending possibly on the particular metal and possibly also on the type and degree of deformation.

Hafnium, on the basis of the present investigation, would appear to be a member of this group. The most reliable lattice parameters seem to be<sup>2</sup>:  $a = 3.1883$ ,  $c = 5.0442$  Å. This gives hafnium a  $c/a$  ratio of 1.58, and therefore that it should have a texture similar to that of the metals listed in the previous paragraph is not unexpected. The most recently reported textures for all four metals, based for the most part on Geiger-counter spectrometer data, are listed in Table I.

TABLE I.—Cold-Rolled Textures of Some Hexagonal Metals with Similar  $c/a$  Ratios

Metal	$c/a$ Ratio	Direction Parallel to Rolling Direction	Angle between Basal Plane and Rolling Plane in Transverse Direction	Ref.
Titanium .	1.60	[10 $\bar{1}$ 0]	30°–50°	1, 3
Zirconium .	1.59	[10 $\bar{1}$ 0]	36°–40°	4, 5
Beryllium .	1.58	[10 $\bar{1}$ 0]	0°–65°	6
Hafnium .	1.58	[10 $\bar{1}$ 0]	25° $\pm$ 2°	Present investigation

## II.—EXPERIMENTAL PROCEDURE

A previous investigation<sup>7</sup> of the preferred orientation of cold-rolled hafnium was hampered by the relatively poor rolling characteristics of the samples studied. These had been sectioned from crystal-bar material and proved rather brittle. However, arc-melted crystal-bar material prepared at the U.S. Bureau of Mines Station at Albany, Oregon, was found to be much more plastic. Two samples of the arc-melted material were supplied to the present authors; one contained approximately 3% and

the other 0.01% zirconium as the principal impurity. The other impurities, in both cases, were reported to be of the order of 500 p.p.m. or less. The reduction possible on the material containing 3% zirconium seemed to be limited only by the rolling equipment available. By using 2-in. rolls and small passes, specimens were rolled to 0.004 in. in thickness (95% reduction) with only minor amounts of edge-cracking. The samples were turned end for end after each pass, but the rolling direction was kept constant. The 0.01% zirconium strip cracked badly at approximately 60–70% total reduction in thickness. This poor rolling capacity may possibly have been due to the presence of dissolved gas as an impurity. It appears that zirconium in solid solution in hafnium does not impair the cold-rolling properties of the latter. As a result of the superior rolling qualities, the investigation described was based on the 3% zirconium material, two sets of samples of which were prepared. One set was rolled to 0.010 in. (approximately 85% reduction) and the other set to 0.004 in. (95% reduction in thickness).

After rolling, the samples were etched in a solution containing by volume: conc. HCl 10, conc. HF 10, conc. HNO<sub>3</sub> 10, H<sub>2</sub>O 70%. Approximately 0.001 in. was etched from each surface of the specimens to avoid undesirable surface effects in the subsequent determinations of preferred orientation.

A Norelco spectrogoniometer, with the Norelco pole-figure fixture and copper  $K\alpha$  radiation, was used to determine the inner 60° of the (0002), (01 $\bar{1}$ 0), and (10 $\bar{1}$ 1) pole figures.<sup>8</sup> As hafnium, because of its high density, is poorly suited for determination of pole figures by transmission methods, and because the very limited amount of material available rendered a laminated reflection sample impractical, the investigation was limited to the inner reflection portion of the pole figures. In all cases, however, the data obtained were enough completely to determine the preferred orientations.

For hafnium, the (0002) and (10 $\bar{1}$ 1) 2 $\theta$  angles are less than 2° apart, and as a result certain spurious peaks, caused by reflections from (10 $\bar{1}$ 1) faces, tend to be seen in the (0002) pole figures. Because of the difficulty involved in trying to eliminate these peaks completely by the use of very small slit systems, which tend to give increased resolution but decrease the intensity of all the peaks to an extremely low level, it was found easier to

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prove their nature geometrically in the pole figures obtained than to try to eliminate them.

In obtaining the data for the pole figures, the samples were rotated completely around an axis normal to the rolling plane at a rate of  $10^\circ/\text{min}$ . Thus, all four quadrants were covered. Successive pole-figure circles were recorded at  $5^\circ$  increments about the radius of the pole figure. The specimens were oscillated continually over a distance of approximately  $\frac{1}{4}$  in. in their own plane at a rate of 60 oscillations/min. in order to obtain an intensity value indicative of a representative area of the sample. In no case were the diffracted intensities greater than 600 counts/sec.—the practical linear counting-rate limit of the tube used—and therefore no correction for counting efficiency was necessary.

Correction factors for tilting were established by using a powdered hafnium sample.<sup>9</sup> The sample was produced

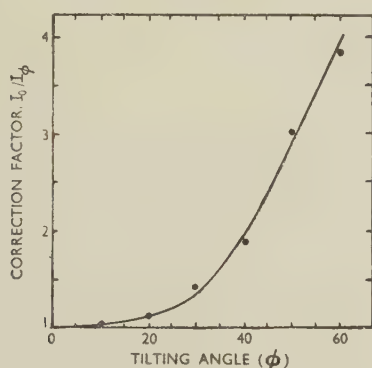


FIG. 1.—Graph of Tilting-Angle Correction Factors.

by making a paste of a 400-mesh, vacuum-annealed hafnium powder with a very small amount of plastic binder and spreading a 0.010-in. layer of the paste evenly on a glass slide. The sample was rotated about an axis normal to the diffracting plane, and intensity values were measured at two different diffracting angles at  $10^\circ$  increments about the tilting axis. The tilting-angle correction factors were calculated and used to correct the pole-figure intensity values subsequently obtained. A graph of the tilting-angle correction factors is plotted in Fig. 1.

### III.—EXPERIMENTAL RESULTS

A set of pole figures for a specimen of cold-rolled strip 0.004 in. thick is shown in Figs. 2(a)–(c). The pole figures for the other samples reduced 95% were substantially identical, and there was no significant difference in the samples reduced 85%. This set of pole figures is, therefore, representative of all the samples examined.

The locations of the spurious areas noted in the (0002) figure are shown as dotted lines. Although these peaks are relatively intense, it is obvious that they are not true orientation peaks, because the peaks which would be associated with them do not appear in the other pole figures.

The scale of the contour lines of the pole figures is in counts/sec., as corrected by a tilting factor.

Small circles in the (0002) pole figure, small squares in

the  $(10\bar{1}0)$  pole figure, and small triangles in the  $(10\bar{1}1)$  pole figure denote the theoretical location of the peaks, assuming a basal rotation of  $25^\circ$  toward the transverse

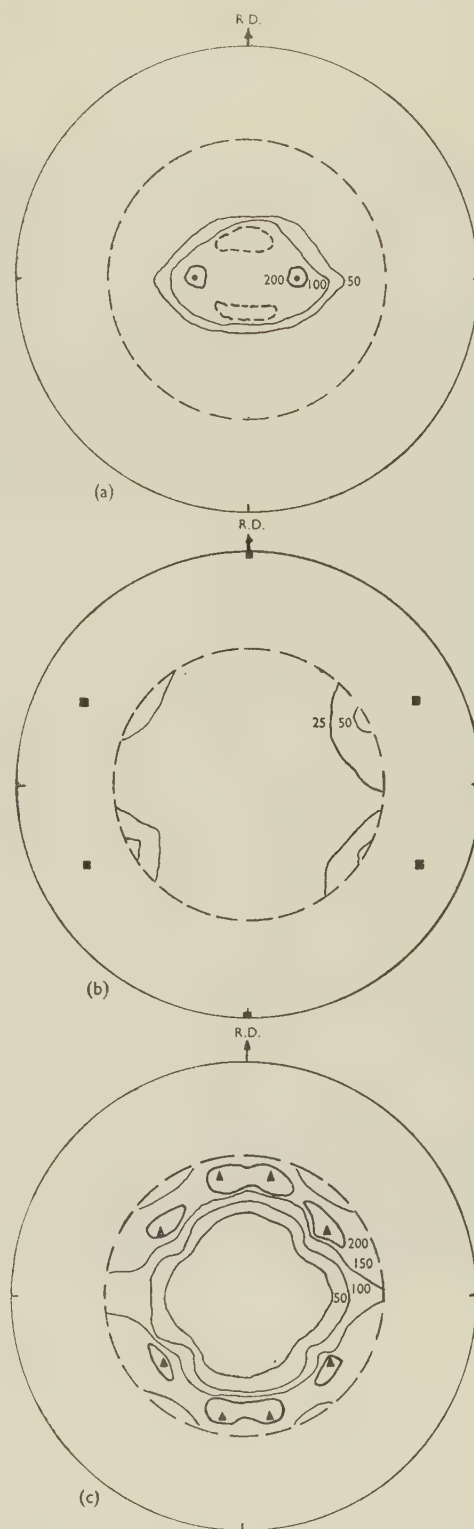


FIG. 2 (a)–(c).—Pole Figures for Hafnium Strip Containing 3% Zirconium Cold Rolled to 95% Reduction in Thickness. (a) (0002). Dotted lines indicate spurious areas; (b)  $(10\bar{1}0)$ ; (c)  $(10\bar{1}1)$ .

direction about an axis in the rolling direction from an ideal (0001)[10 $\bar{1}$ 0] texture.

The symmetry of the (10 $\bar{1}$ 0) and (10 $\bar{1}$ 1) pole figures is well defined, indicating that the deformed sample assumes a [10 $\bar{1}$ 0] direction. The (0002) peak appears to lie at an angle of 25° with the rolling plane rotated about the rolling direction, which, as indicated, is the [10 $\bar{1}$ 0] direction. The exact angle of rotation cannot be absolutely determined because of the possibility of very small variations in the tilting-angle intensity corrections and also because of the width of the peak itself. From the diagram, however, it would seem logical to assume that the rotation is 25°  $\pm$  2°.

#### IV.—SUMMARY

(1) A sample of arc-melted hafnium containing 3% zirconium, cold rolled to 95% reduction in thickness, showed a similar texture to the other hexagonal metals—titanium, zirconium, and beryllium—of similar  $c/a$  ratio.

(2) This texture, for the case of the arc-melted cold-rolled hafnium, can be said to be (0001)[10 $\bar{1}$ 0] rotated 25°  $\pm$  2° about the rolling direction.

(3) The explanation of the mechanism of this deformation texture is undoubtedly similar to that described for the other metals of similar  $c/a$  ratio.<sup>10, 11</sup>

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## PHOTOMICROGRAPHS OF COPPER-GERMANIUM ALLOYS

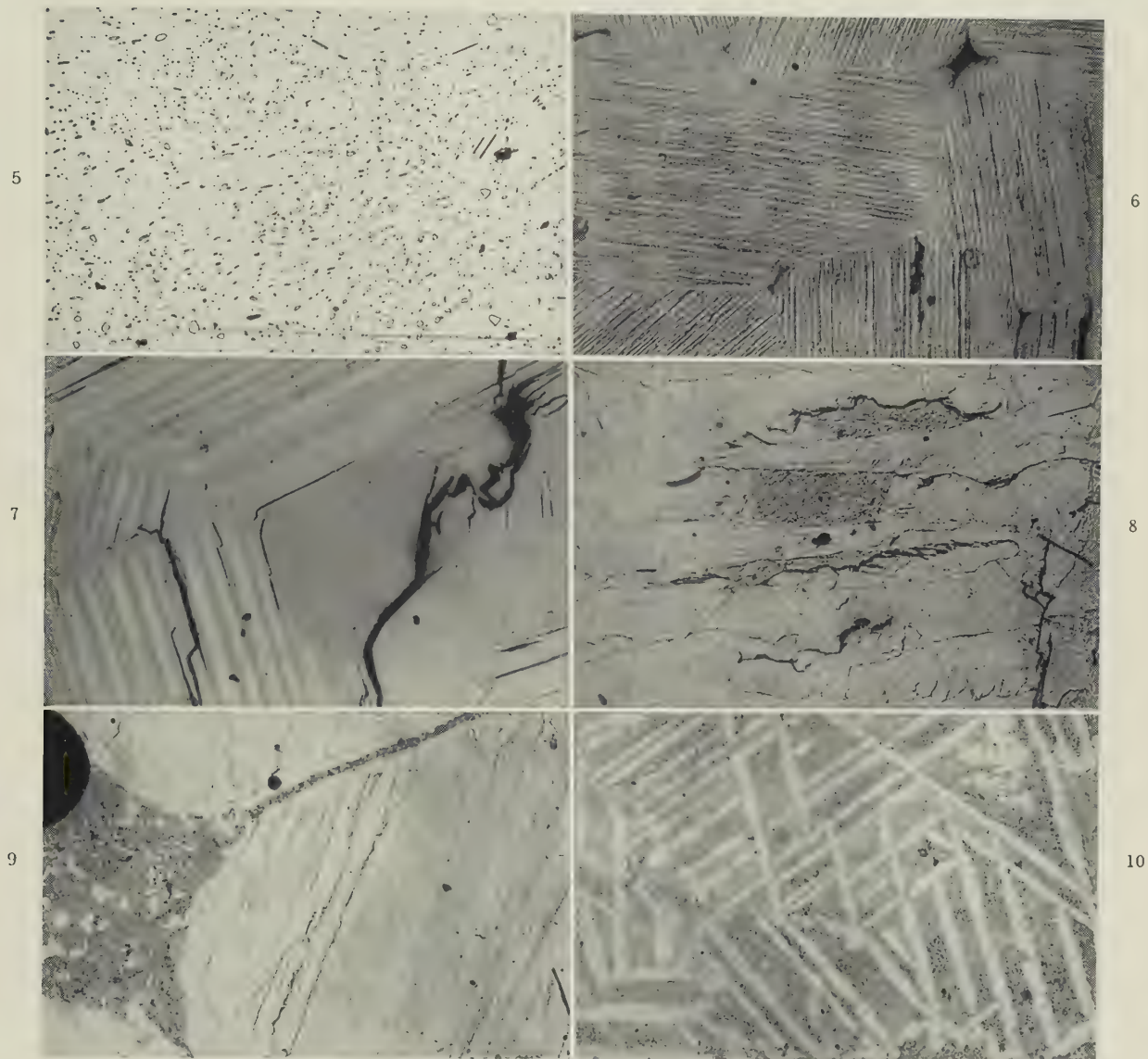
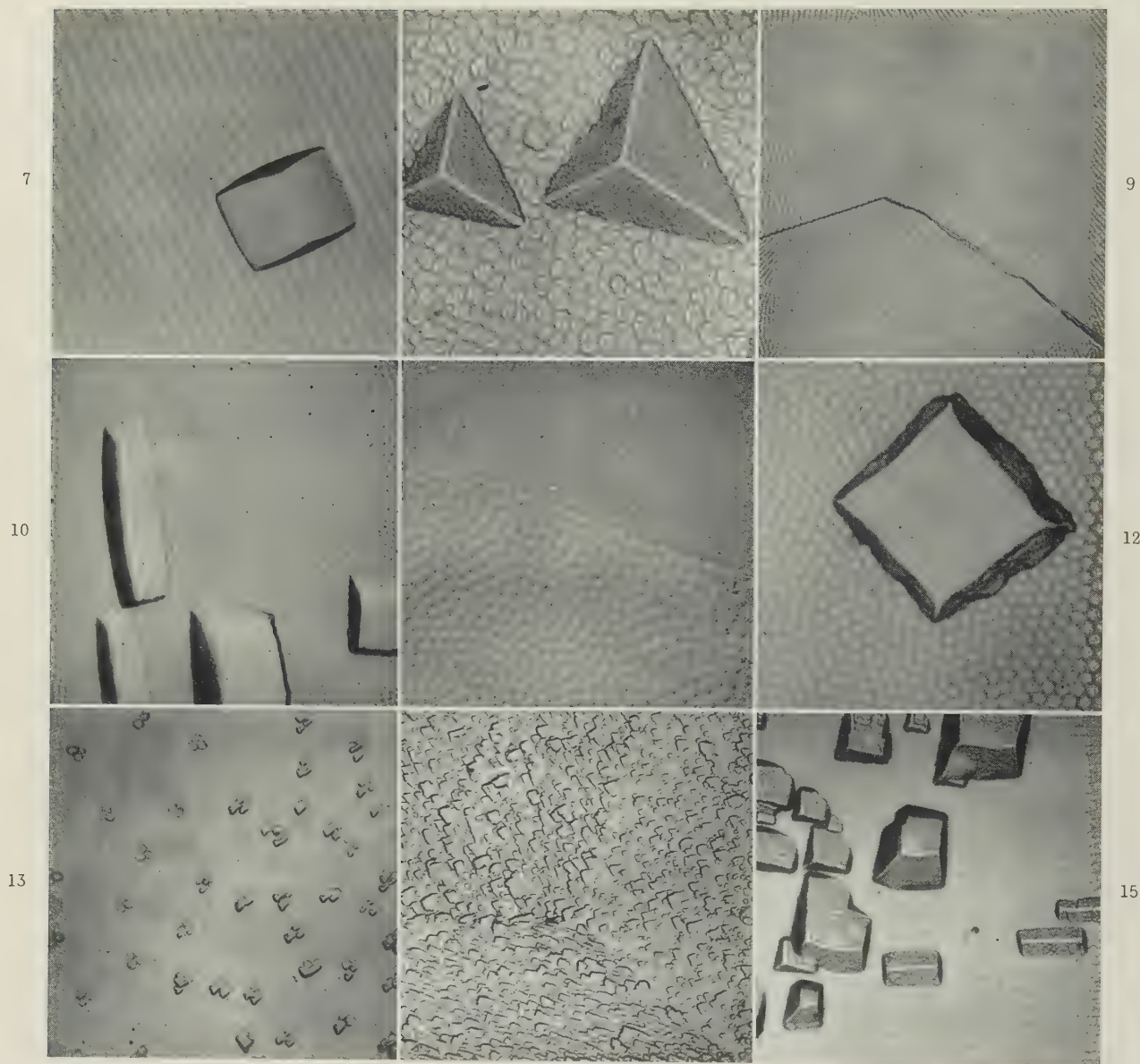


FIG. 5.—26.0 at.-% Ge. Annealed at 602° C. and quenched.  $\epsilon$  + germanium.  $\times 140$ .  
 FIG. 6.—24.0 at.-% Ge. Annealed at 708° C. and rapidly quenched.  $\epsilon_1$  and chilled liquid.  $\times 70$ .  
 FIG. 7.—24.0 at.-% Ge. Annealed at 630° C. and rapidly quenched.  $\epsilon$  +  $\epsilon_1$ .  $\times 70$ .  
 FIG. 8.—23.5 at.-% Ge. Annealed at 732° C. and slowly quenched.  $\epsilon_1$ .  $\times 120$ .  
 FIG. 9.—24.0 at.-% Ge. Annealed at 708° C. and slowly quenched.  $\epsilon_1$  + chilled liquid.  $\times 75$ .  
 FIG. 10.—26.0 at.-% Ge. Annealed at 692° C. and quenched.  $\eta$ .  $\times 60$ .

## PSEUDO-SUBGRAIN STRUCTURES IN ALUMINIUM

8



14

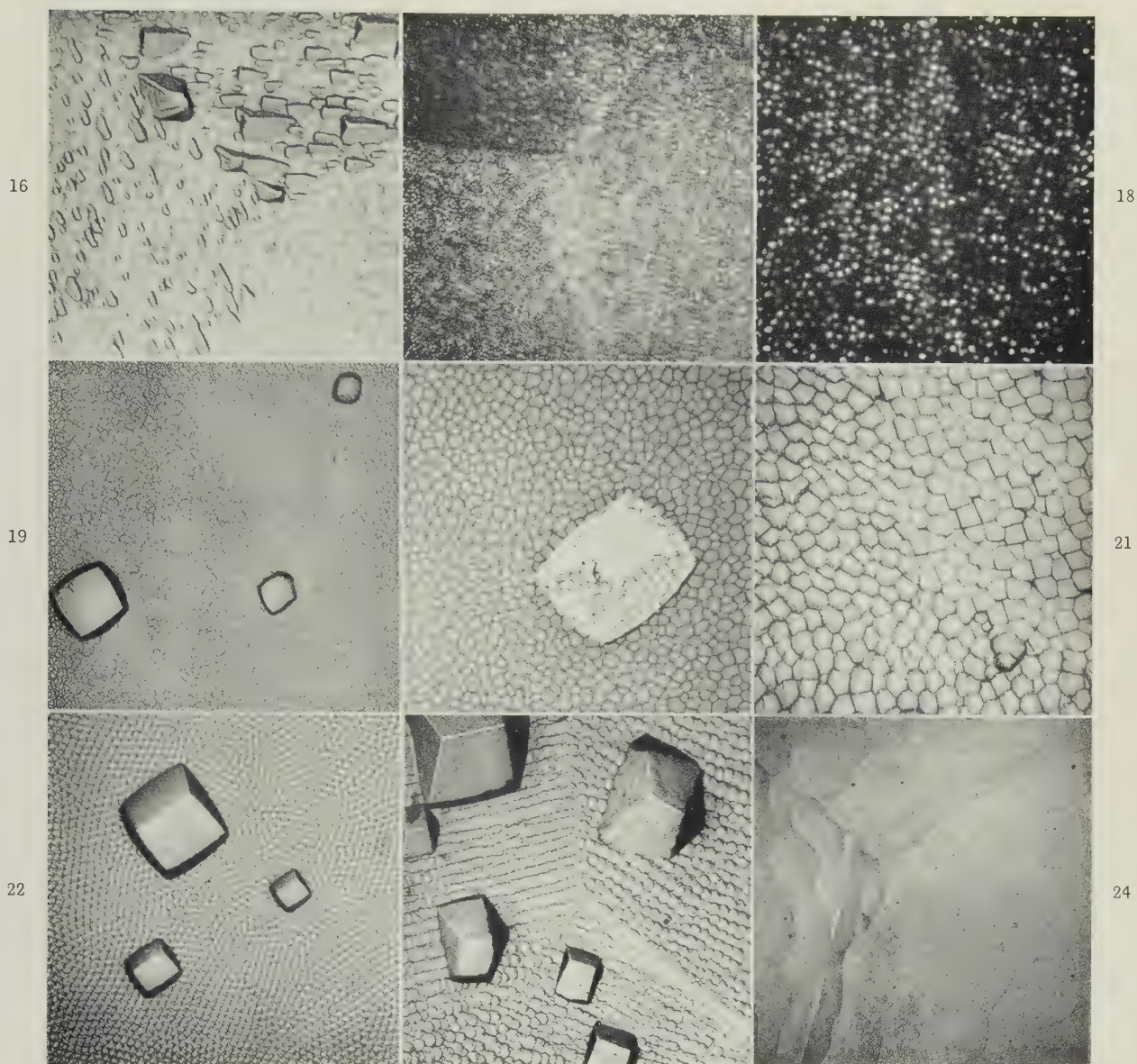
FIGS. 7-14.—Perchloric Acid-Alcohol Bath.

FIG. 7.—Furrow structure on near-(110) face.  $\times 20,000$ .FIG. 8.—Granular modification of furrow structure on near-(111) face.  $\times 20,000$ .FIG. 9.—15 V.,  $0^{\circ}$  C. Furrow structure at ternary grain boundary.  $\times 10,000$ .FIG. 10.—25 V.,  $0^{\circ}$  C. Transition to dotted structure. Shadowed replica.  $\times 10,000$ .FIG. 11.—50 V.,  $0^{\circ}$  C. Dotted structure on one grain.  $\times 10,000$ .FIG. 12.—70 V.,  $-18^{\circ}$  C. Fully developed globular structure.  $\times 10,000$ .FIG. 13.—50 V.,  $-18^{\circ}$  C. Globules in groups of three.  $\times 7000$ .FIG. 14.—70 V.,  $0^{\circ}$  C. Fine crystallographic etching.  $\times 10,000$ .FIG. 15.—Perchloric Acid-Acetic Anhydride Bath. 20 V.,  $+18^{\circ}$  C. Furrow structure.  $\times 10,000$ .



## PSEUDO-SUBGRAIN STRUCTURES IN ALUMINIUM

17



23

FIG. 16.—Perchloric Acid-Acetic Anhydride Bath. 50 V., +18° C. Granular structure with etching.  $\times 10,000$ .

FIGS. 17-22.—Phosphoric Acid-Alcohol Bath.

FIG. 17.—10 V., +18° C. Pore structure of oxide film.  $\times 10,000$ .

FIG. 18.—30 V., +18° C. Pore structure of oxide film.  $\times 10,000$ .

FIG. 19.—10 V., +18° C. Deoxidized.  $\times 10,000$ .

FIG. 20.—50 V., +18° C. Deoxidized. "Double-film" effect.  $\times 10,000$ .

FIG. 21.—90 V., +18° C. Deoxidized in 1% HF.  $\times 10,000$ .

FIG. 22.—Breakdown voltage exceeded.  $\times 10,000$ .

FIGS. 23-24.—Hydrofluoric Acid-Alcohol Bath.

FIG. 23.—45 V., +18° C. Deoxidized.  $\times 10,000$ .

FIG. 24.—5 V., +18° C. Deoxidized. Coarse cell structure.  $\times 7000$ .

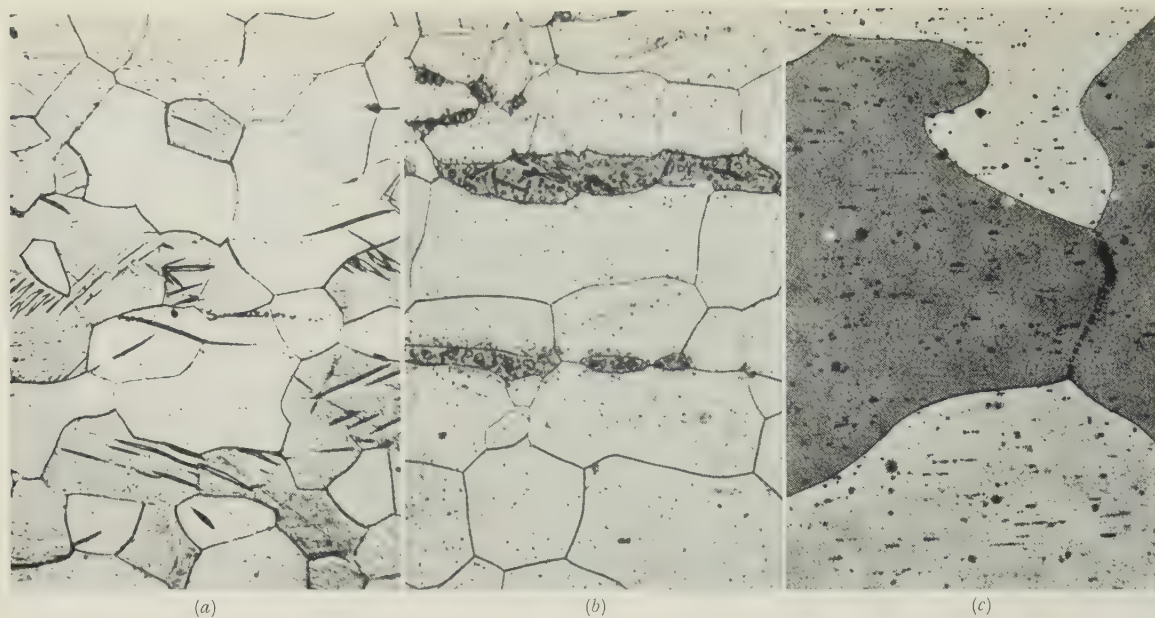


FIG. 11.—Microstructures and A.S.T.M. Grain-Size of Annealed Binary Magnesium-Lithium Alloys (Grain-Size by Comparison Method). Acetic acid-Picral etch. (a) 4% Li, grain-size 7.0.  $\times 300$ . (b) 6% Li, grain-size 5.5.  $\times 300$ . (c) 11% Li, grain-size 0.  $\times 75$ .

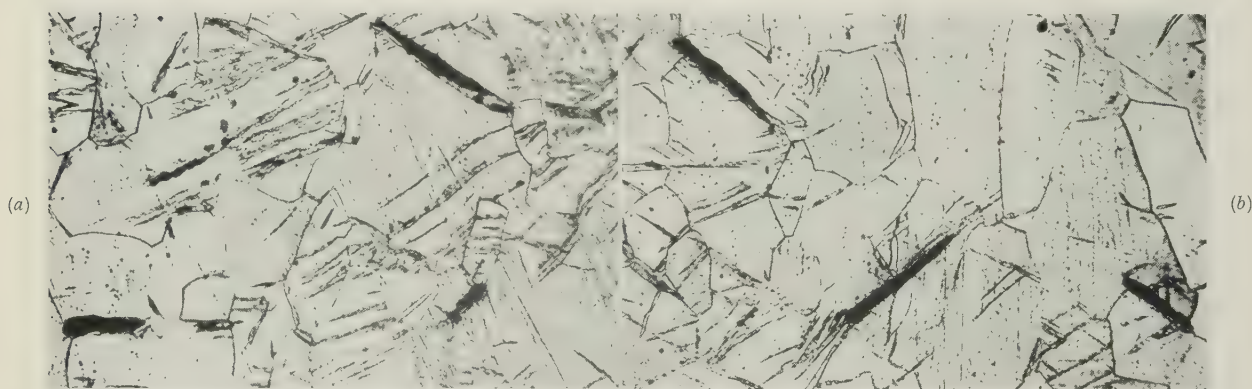


FIG. 12.—Cracking Behaviour of Magnesium-4% Lithium Alloy. (a) Crack formation on previously formed twin. Stretched 31.7% at room temperature and 0.05 in./min. (b) Illustrating difficulty of crack propagation through unfavourably oriented grains. Stretched 20% at room temperature and 0.05 in./min.

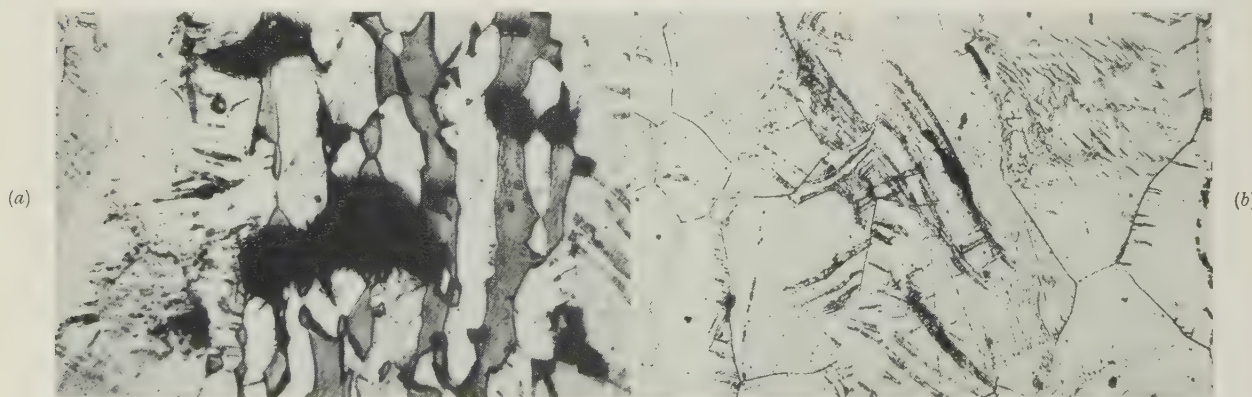


FIG. 13.—Comparison of Cracking Behaviour of Magnesium-6% Lithium Alloy (a) in Vicinity of a Two-Phase Region, and (b) in a Single-Phase Region. Stretched 39.4% at  $-110^{\circ}\text{F.}$  ( $-80^{\circ}\text{C.}$ ) and 0.05 in./min.



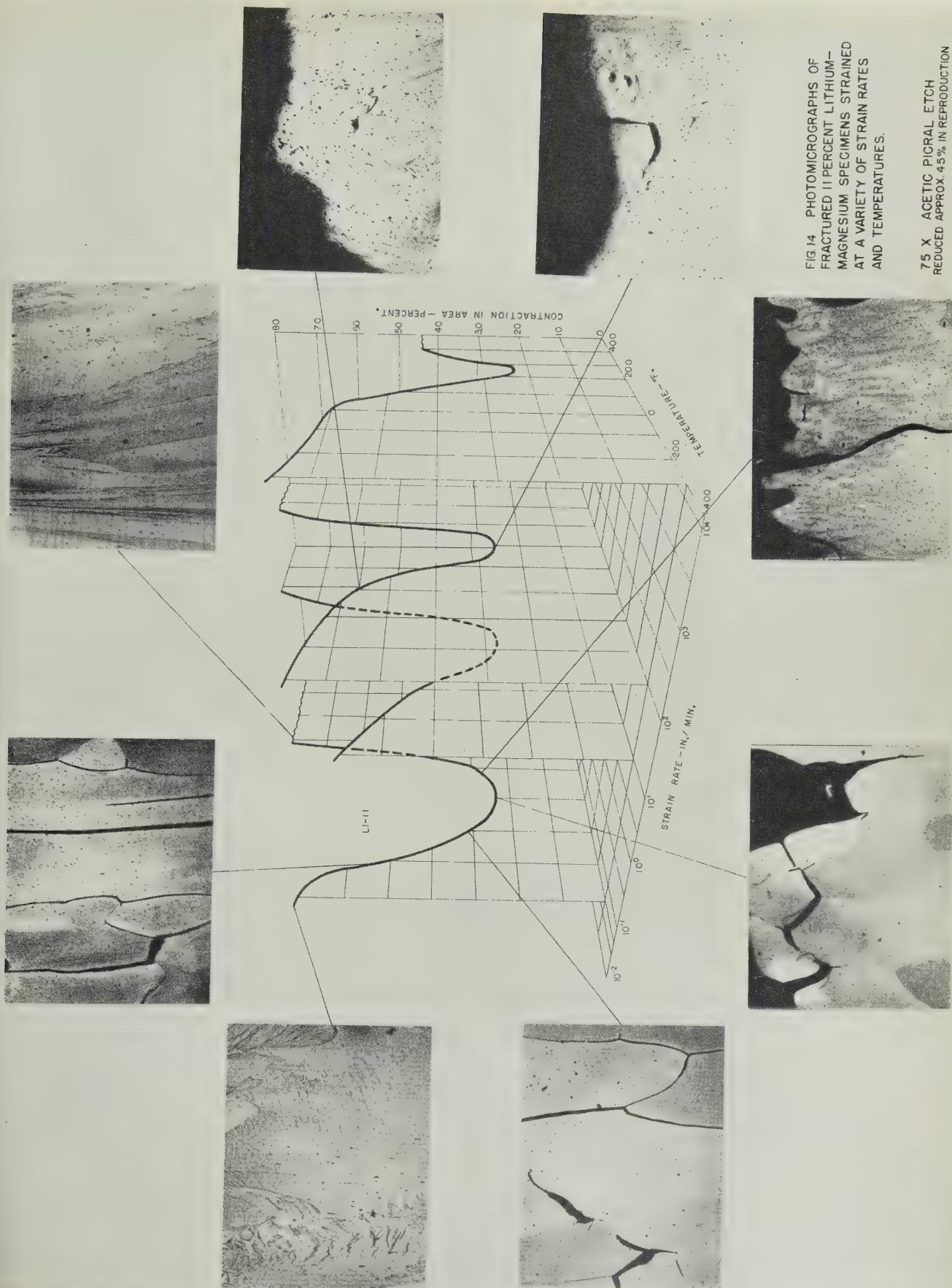
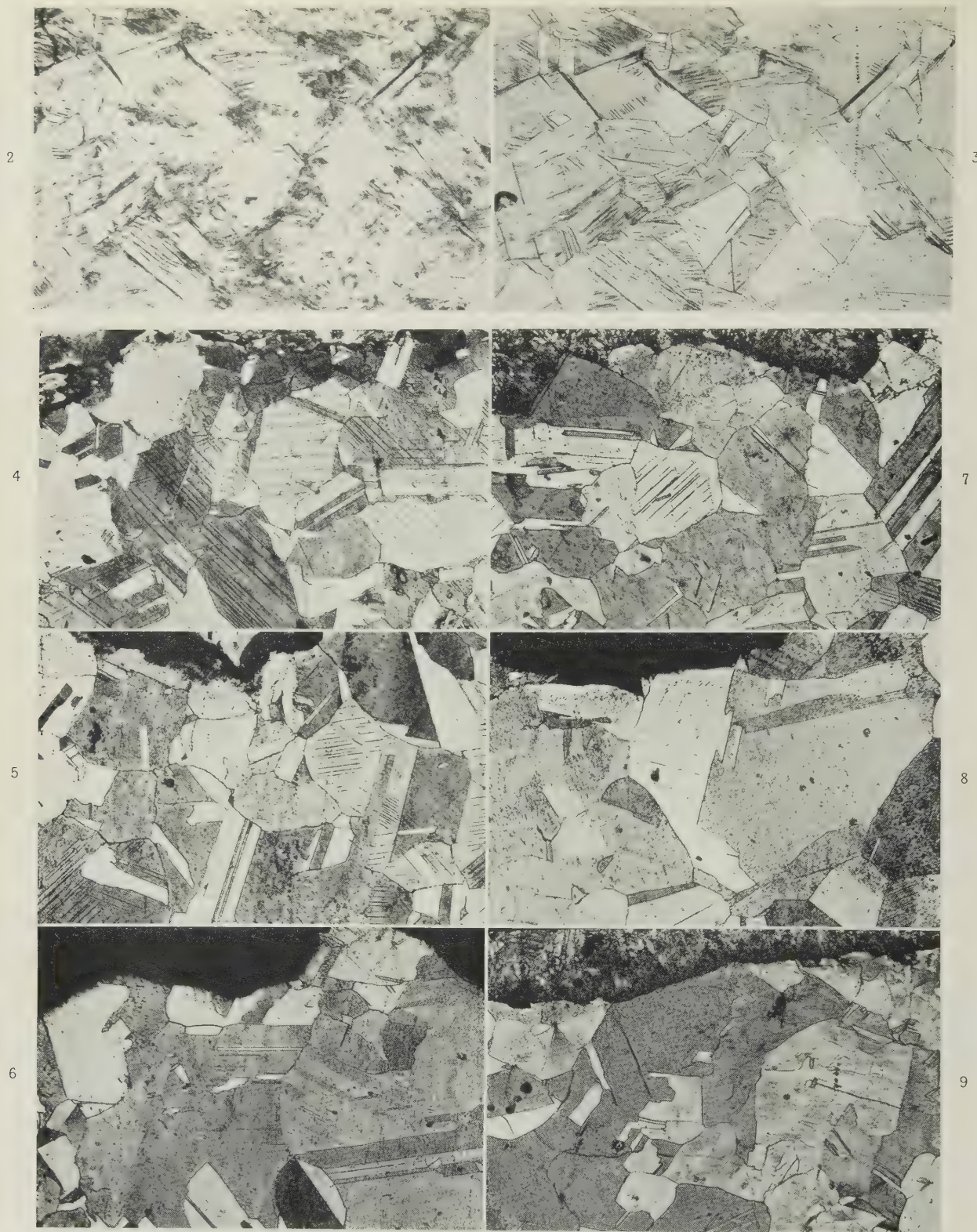


FIG 14 PHOTOMICROGRAPHS OF  
FRACTURED LITHIUM-MAGNESIUM  
SPECIMENS STRAINED  
AT A VARIETY OF STRAIN RATES  
AND TEMPERATURES.

75 X ACETIC PICRAL ETCH  
REDUCED APPROX 45% IN REPRODUCTION



## MICROSTRUCTURES OF FRACTURED COPPER FATIGUE SPECIMENS



FIGS. 2 and 3.—Surface Microstructures of Rotating-Cantilever Specimens, Indicating Correspondence of Striations with Slip Bands Produced by Cyclic Stress.  $\times 200$ .

FIG. 2.—As fatigued at  $\pm 11,000$  lb./in.<sup>2</sup>, 6000 c./m. (specimen No. 4).

FIG. 3.—Same area as Fig. 2, after electropolishing and etching.

FIGS. 4-9.—Longitudinal Sections of Rotating-Cantilever Specimens, Showing Decrease in Number of Striations with Increasing Stress and Increasing Frequency.  $\times 150$ .

FIG. 4.— $\pm 14,000$  lb./in.<sup>2</sup>, 21 c./m. (specimen No. 1).

FIG. 5.— $\pm 16,000$  lb./in.<sup>2</sup>, 21 c./m. (specimen No. 2).

FIG. 6.— $\pm 20,000$  lb./in.<sup>2</sup>, 21 c./m. (specimen No. 3).

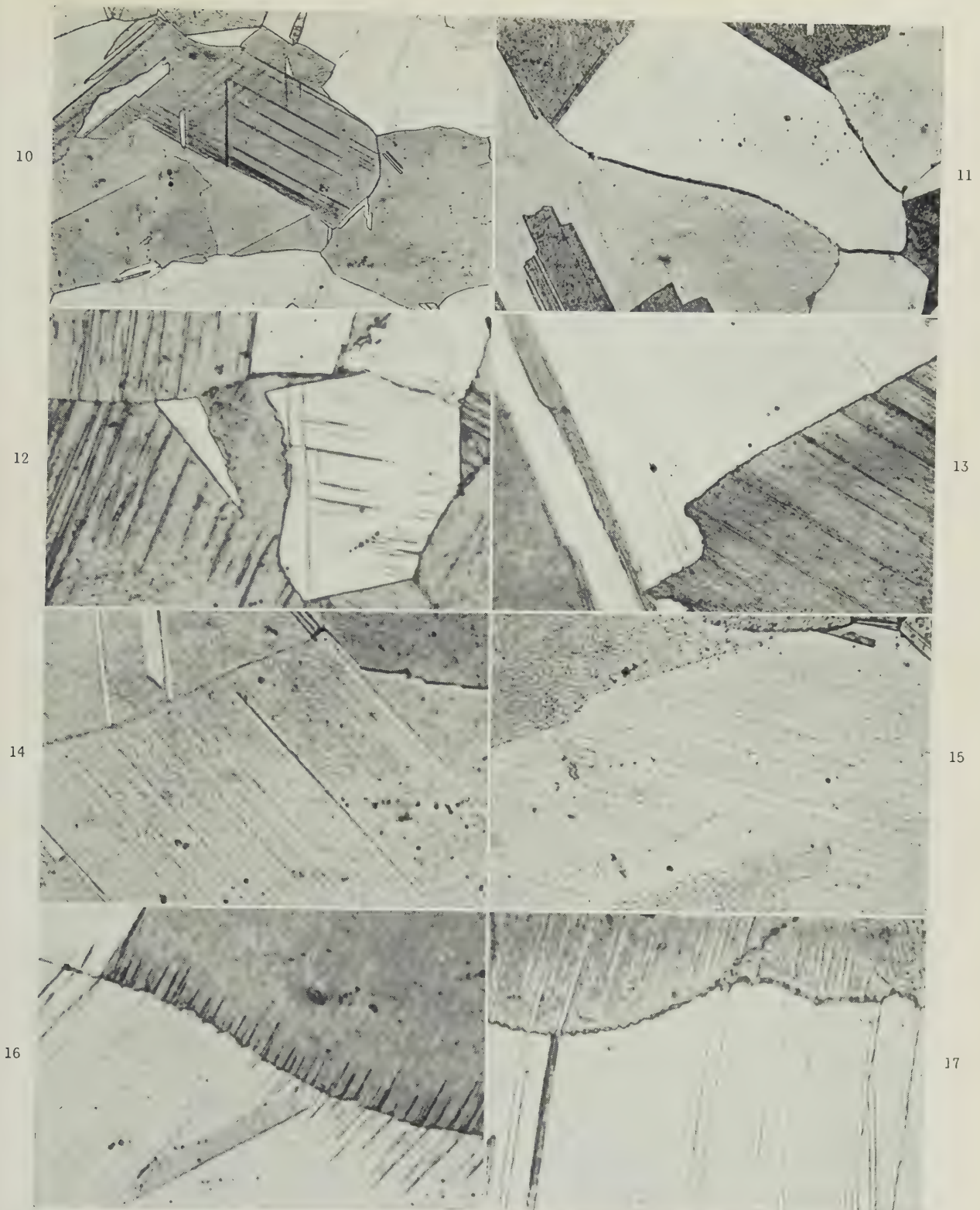
FIG. 7.— $\pm 14,000$  lb./in.<sup>2</sup>, 6000 c./m. (specimen No. 5).

FIG. 8.— $\pm 16,000$  lb./in.<sup>2</sup>, 6000 c./m. (specimen No. 7).

FIG. 9.— $\pm 20,000$  lb./in.<sup>2</sup>, 6000 c./m. (specimen No. 8).

All etched in acid ferri chloride solution.





FIGS. 10 and 11.—Longitudinal Sections of Push-Pull Specimens, Showing Decrease in Number of Striations with Increasing Stress.  $\times 350$ .

FIG. 10.— $\pm 9000$  lb./in.<sup>2</sup>, 2000 c./m. (specimen No. 10).

FIG. 11.— $\pm 16,000$  lb./in.<sup>2</sup>, 2000 c./m. (specimen No. 11).

FIGS. 12-15.—Longitudinal Sections of Rotating-Cantilever Specimens, Showing Decrease in Intensity of Striations with Increasing Stress.  $\times 1000$ .

FIG. 12.— $\pm 11,000$  lb./in.<sup>2</sup>, 6000 c./m. (specimen No. 4).

FIG. 13.— $\pm 15,000$  lb./in.<sup>2</sup>, 6000 c./m. (specimen No. 6).

FIG. 14.— $\pm 20,000$  lb./in.<sup>2</sup>, 6000 c./m. (specimen No. 8).

FIG. 15.— $\pm 25,000$  lb./in.<sup>2</sup>, 6000 c./m. (specimen No. 9).

FIGS. 16-18.—Boundary Effects of Striations in Rotating-Cantilever Specimens.  $\times 1000$ .

FIG. 16.— $\pm 11,000$  lb./in.<sup>2</sup>, 6000 c./m. (specimen No. 4). Concentration at grain boundary, boundary crossing, and serrated boundary.

FIG. 17.— $\pm 14,000$  lb./in.<sup>2</sup>, 21 c./m. (specimen No. 1). Serrated boundary.

All etched in acid ferric chloride solution.

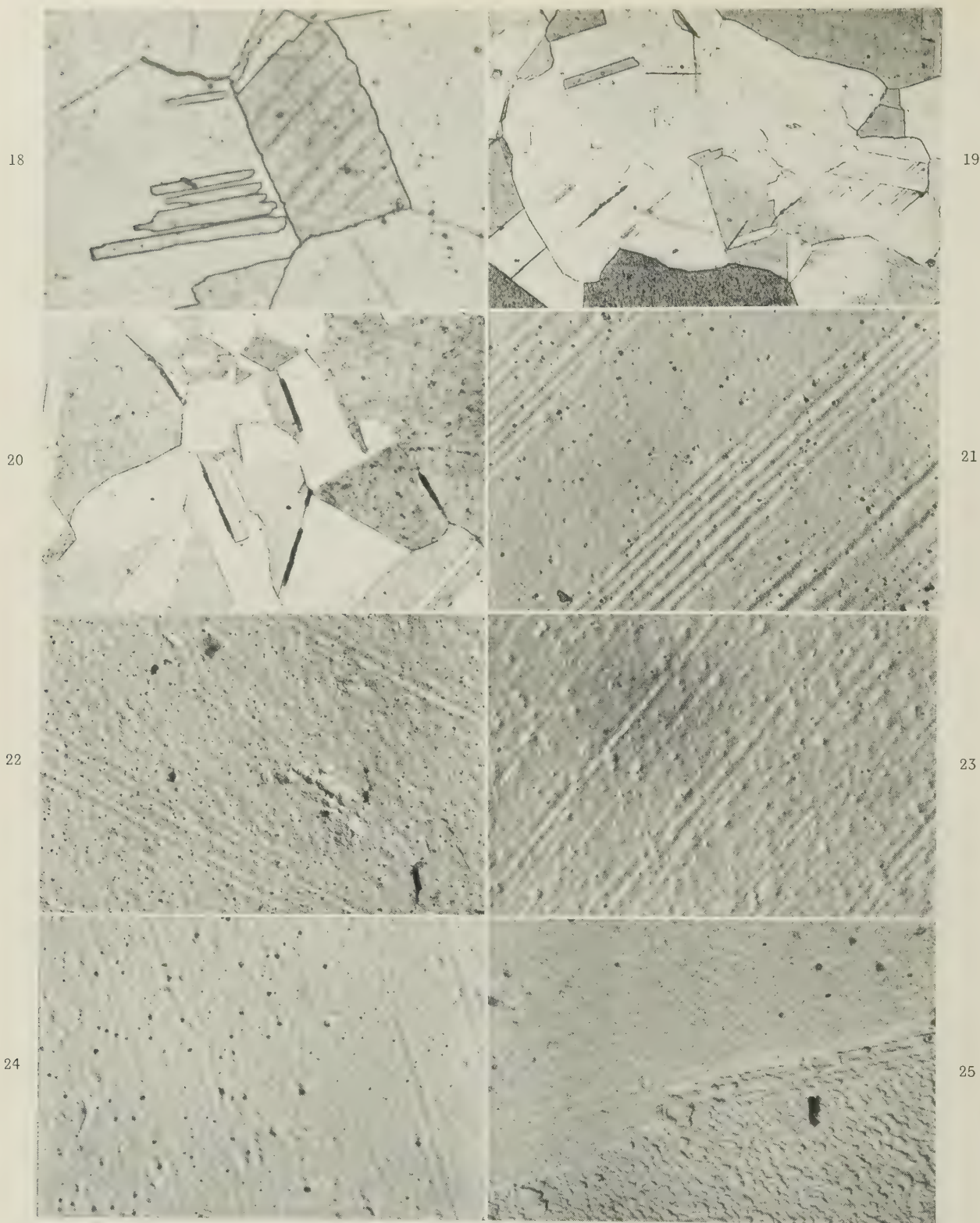


FIG. 18.— $\pm 14,000$  lb./in.<sup>2</sup>, 21 c./m. (specimen No. 1). Kinked boundary of annealing twin.

FIGS. 19 AND 20.—Modes of Occurrence of Persistent Slip Bands in a Rotating-Cantilever Specimen Cycled to 10% of Its Life at  $\pm 10,000$  lb./in.<sup>2</sup> (specimen No. 12).  $\times 150$ .

FIG. 19.—Persistent slip bands associated with striations.

FIG. 20.—Persistent slip bands associated with annealing-twin boundaries.

FIGS. 21-24.—Electron Micrographs of Striations Developed at Various Stresses in 6000 c./m. Rotating-Cantilever Specimens, Showing Clustering of Lines at Low Stresses.  $\times 12,000$ .

FIG. 21.— $\pm 11,000$  lb./in.<sup>2</sup> (specimen No. 4).

FIG. 23.— $\pm 20,000$  lb./in.<sup>2</sup> (specimen No. 8).

FIG. 22.— $\pm 15,000$  lb./in.<sup>2</sup> (specimen No. 6).

FIG. 24.— $\pm 25,000$  lb./in.<sup>2</sup> (specimen No. 9).

FIG. 25.—Electron Micrograph of Striations Running Parallel to an Annealing-Twin Boundary, and Contiguous with It (specimen No. 2).  $\times 8000$ .

All etched in acid ferric chloride solution.



# STRESS-CORROSION OF WROUGHT TERNARY AND COMPLEX ALLOYS OF THE ALUMINIUM-ZINC-MAGNESIUM SYSTEM \*

1737

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## SYNOPSIS

Previous investigations of stress-corrosion in alloys of the aluminium-zinc-magnesium type are briefly reviewed. Attempts to establish optimum proportions of zinc and magnesium, together with other added elements, have been based on tests in bending either at a fixed strain without reference to elastic properties, or under an applied stress bearing a fixed relation to the elastic limit. No information is available on the behaviour of any one alloy over a range of stresses.

The object of the present investigation was to develop a method of test under closely defined conditions and to use this to establish stress/time-to-failure relationships for a number of alloys. New equipment was designed for direct-tension stressing, using spring loading combined with a dash-pot device to absorb the energy released by the breaking of a stressed specimen. By this means several units working at high loading could be installed in a small space with exact control of environment.

The apparatus was used in the first place to study wrought ternary alloys with 5-9% zinc and 0.4-2.8% magnesium, made from high-purity metals. In these, stress-cracking occurs at comparatively low stresses, time-to-failure diminishing with increase in zinc + magnesium content. Complex alloys with 7% zinc and 2½% magnesium, with smaller amounts of copper, manganese, and chromium, separately and combined, were prepared in duplicate, one series from a commercial grade of aluminium and the other from high-purity metal, and stress/time-to-failure relationships were established for 16 alloys, each in two conditions of heat-treatment.

Some increased resistance to stress-corrosion is conferred by the iron and silicon in the commercial-purity metal; this can be ascribed mainly to grain refinement. Copper has been shown to be beneficial because it results in anodic areas developing at grain centres as well as at grain boundaries, while chromium diminishes stress-corrosion tendencies by producing an elongated grain structure.

Comparison of specimens subjected to the same corrosive environment, with and without stress, showed no evidence of physical change due to the application of stress at any time before the actual stress-corrosion fracture.

## I.—INTRODUCTION

THE Eleventh Report to the Alloys Research Committee of the Institution of Mechanical Engineers prepared by Rosenhain, Archbutt, and Hanson,<sup>1</sup> in 1921, recorded a tensile stress exceeding 40 tons/in.<sup>2</sup> in a wrought aluminium alloy containing 20% zinc, along with magnesium, copper, and manganese, but rejected this type of alloy on account of season-cracking.

Recognition of the outstanding mechanical properties of aluminium-zinc-magnesium alloys at lower ranges of zinc content was due to work carried out by Sander and Meissner<sup>2</sup> in 1926, which also indicated the significance of corrosion as a factor in cracking under prolonged stressing. In spite of intensive studies over the past 30 years, leading to the wide adoption by the aircraft industry of alloys of this basic type, relationships between composition, stress level, and cracking in service are still undefined.

The first objective of the present investigation was to develop an experimental method of establishing quantitatively the stress-corrosion performance of any one

alloy. A comparison was then made of stress/time-to-failure relationships for a number of ternary aluminium-zinc-magnesium alloys, and for one selected ternary alloy with additions of copper, chromium, and manganese, separately and together. Some general deductions could thus be made on the influence of composition on the safe level of stressing, although insufficient work has been carried out to establish an optimum composition.

## II.—PREVIOUS WORK

The behaviour under direct tensile stress of ternary wrought alloys made from high-purity metals has been previously studied by Hérenghuel and Lacombe,<sup>3</sup> who found that, with a combined total of more than 9% of zinc + magnesium, brittleness developed on ageing, specimens displaying an intercrystalline fracture in tension. In a later paper, Hérenghuel<sup>4</sup> showed that alloys which broke in a ductile manner under rapid application of stress fractured in a brittle intercrystalline manner when submitted to a lower sustained stress. Furthermore, alloys made from high-purity aluminium

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failed in a shorter time than those made from commercial-purity metal containing iron and silicon. For example, an alloy with 6% zinc and 2% magnesium, stressed at 30 kg./mm.<sup>2</sup>, failed in two days when made from high-purity aluminium, or in 39 days when made from commercial-purity aluminium. This brittle fracture was ascribed to the weakening of intercrystalline cohesion and was termed "decohesion".

All published investigations of stress-corrosion in more-complex wrought alloys based on the aluminium-zinc-magnesium system record the use of bending methods of one kind or another. German investigators<sup>5-11</sup> adopted a modified form of the U-shaped specimen of Rosenhain and Archbutt.<sup>12</sup> In the procedure described by Wassermann<sup>11</sup> a sheet specimen 15 × 140 mm. was bent over a radius of 8 times the sheet thickness through slightly more than 180°, the two arms being riveted together. Loops thus formed were mounted on rods in a D.V.L. machine, which carried out an automatic cycle of immersion in a 3% solution of sodium chloride and drying in the open air. The time to fracture was recorded and specimens unfractured after 100 days were regarded as resistant to stress-corrosion.

The maximum fibre stress applied in this loop test is not capable of exact calculation, because specimens are deformed both elastically and plastically, and indeed there will generally be significant plastic deformation at the position of maximum fibre stress. However, the method has been employed primarily as a sorting test, using a statistical assessment of the percentage of specimens fractured. Wassermann made the important observation that for each 10° rise in temperature in the range 10°–70° C., time to failure is shortened by more than a factor of 10.

Referring to individual investigations, Hansen, Mühlenbruch, and Seemann<sup>5, 6</sup> found that alloys with a total of not more than 6% (zinc + magnesium) were resistant to stress-corrosion in all conditions of thermal treatment. However, because of inadequate strength further studies were instituted outside this range, and two alloys containing, respectively, 6% zinc + 2% magnesium, and 4% zinc + 2% magnesium, with manganese in the range of 0.5–0.8%, proved to have acceptable mechanical properties and to be free from susceptibility to stress-corrosion if aged either at room temperature or artificially at temperatures exceeding 100° C. Lower temperatures of ageing induced marked susceptibility to cracking. Siebel and Vosskühler<sup>7, 8</sup> also reported that the tendency to stress-corrosion increased with increase in the total zinc + magnesium content, and showed that for good stress-corrosion performance the alloys should be aged either at room temperature or at 125° C., intermediate temperatures being detrimental. They then selected an alloy with 4.5% zinc and 3.5% magnesium for detailed study. Copper contents of 0.1–0.6%, manganese of 0.1–0.5%, and chromium of 0.1–0.4% were shown to have a favourable influence, and alloys containing all three elements were recommended, specimens being uncracked after 100 days' test. Bungalow and Schaitberger,<sup>9, 10</sup> using a slightly modified form of test-piece, made further studies of alloys based on 4.5% zinc + 3.5% magnesium. In the room-temperature-aged condition, 0.15% copper and 0.2–0.3% chromium prevented stress-corrosion failure. Artificial ageing, unless carried out above 100° C., produced

susceptibility to stress-corrosion except in the presence of copper and vanadium. In pseudo-binary alloys of the Al-MgZn<sub>2</sub> system with up to 8% MgZn<sub>2</sub>, stress-corrosion tendencies increased with increase in MgZn<sub>2</sub> content, while copper and vanadium additions proved beneficial.

Dix<sup>13</sup> gave some results of stress-corrosion studies on the American 75S alloy with minor variations in composition, using experimental methods described by Sager, Brown, and Mears.<sup>14</sup> Two examples of these are a constant-stress method in which the sheet sample, supported at its ends, was subjected to two-point loading, and a constant-deflection method in which it was sprung into an arc by placing the ends in parallel fixed slots. In the former, the load was adjusted, and in the latter, the specimen length, but both methods employed a predetermined fibre-stress based on calculation from established formulae for elastic deformation. Dix employed laboratory accelerated tests, including one in which the specimens were immersed in boiling 6% sodium chloride solution for 400 hr., but based his findings in the main on the results of atmospheric exposure at inland and sea-coast locations, and immersion in the sea. All these tests were of the "go, no-go" variety and were operated at 75% of the yield stress. The 75S alloy containing chromium was stated to show only 7% of failures by stress-corrosion cracking in a total of 5000 tests.

The work gave no indication of safe levels of stressing for the various alloy compositions, and for a number of reasons the methods were of insufficient accuracy to do so. For example, under prolonged loading at 75% of the yield stress, creep would affect the arc of bending, and thus the stress level, in the constant-load method, while relaxation would have an even more serious effect on stress in the constant-deflection method. Furthermore, in carrying out testing in the open air the very considerable effect of temperature variation, previously referred to by Wassermann, was completely ignored, as was also the humidity factor, which is so important in all corrosion processes.

### III.—SCOPE OF INVESTIGATION

The present investigation was concerned firstly with the experimental measurement of the stress/time-to-failure relationship. Only after such a method had been established and tested was it possible to make a real assessment of the effect of varying composition on stress-corrosion behaviour. The apparatus was designed to meet the following requirements:

- (1) To avoid the many errors associated with bend procedures, particularly at high stress levels, direct tensile stresses should be applied.

- (2) To avoid possible errors associated with the micro-structural condition of miniature test-pieces, the apparatus should be capable of testing standard tensile test-pieces of 0.5 × 0.050 in. cross-section.

- (3) To ensure constant conditions of exposure, specimens under test should be enclosed in a cabinet providing constant temperature and humidity.

- (4) To provide an adequate scale of experimentation the apparatus should cater for the simultaneous testing of 24 specimens.

Alloys were studied in the form of sheet. It was, of course, realized that these materials are normally used



either as extruded bar or as clad sheet, the latter being protected cathodically against stress-corrosion. Bare unprotected sheet has little practical application. However, extruded bar varies in structure and properties from end to end and from surface to interior, and would have been quite unsuitable for an investigation in which large numbers of test-pieces were required with the closest possible uniformity of structure. On the other hand, with an appropriate rolling and annealing sequence, sheet can readily be prepared which, after heat-treatment, is uniform and consistent throughout.

Nine ternary alloys, denoted Series I, were prepared from raw materials of the highest purity. Compositions are listed in Table I, and their position in relation to the phase fields of the equilibrium diagram at 200° C. are shown in Fig. 1. The solid lines are the phase boundaries according to Fink and Willey,<sup>15</sup> the phases being:  $\alpha$

dolfo,<sup>18</sup> from a study of Köster's work,<sup>19</sup> considered might be ( $\alpha + Z$ ). However, phases actually identified in X-ray studies, outside the scope of the present paper, confirm the diagram of Fink and Willey.

More-complex alloys, Series II and Series III, also listed in Table I, were based on the ternary alloy with 7% zinc and 2½% magnesium, which approximates to the composition shown in an earlier investigation<sup>20</sup> to be the optimum, after taking into consideration not only the mechanical properties of the heat-treated wrought alloy, but also the need to reduce to a minimum the tendency to segregation in casting, and to attain the widest possible temperature range of hot working. Other alloying elements were those normally added to industrial alloys, i.e. copper, manganese, and chromium. Both series of alloys were repeated using commercial aluminium of 99.8% purity.

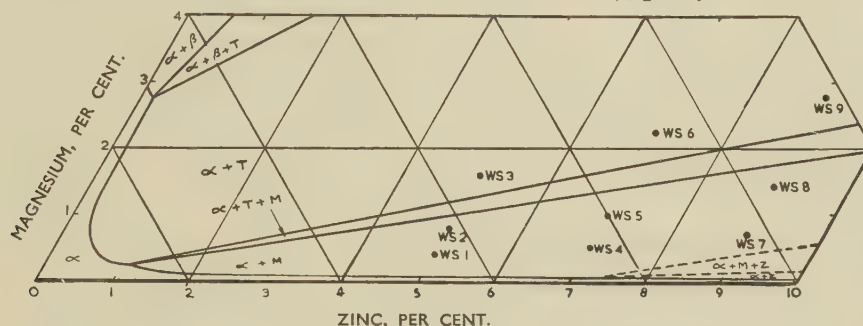


FIG. 1.—Constitutional Diagram for the System Aluminium-Zinc-Magnesium at 200° C.

aluminium solid solution,  $\beta$  or  $\text{Mg}_2\text{Al}_3$ ,  $T$  or  $\text{Mg}_3\text{Zn}_3\text{Al}_2$ , and  $M$  or  $\text{MgZn}_2$ . The dotted lines show the tentative boundaries for the  $Z$  or  $\text{MgZn}_5$  phase proposed by Hume-Rothery *et al.*<sup>16, 17</sup> Three alloys were chosen to fall

TABLE I.—Composition of the Alloys.

	Alloy	Zn, %	Mg, %	Cu, %	Mn, %	Cr, %	Fe, %	Si, %
SERIES I: High-purity base	WS1	5.03	0.39	...	...	...	0.012	0.03
	WS2	5.24	0.85	...	...	...	0.010	0.02
	WS3	4.78	1.54	...	...	...	0.011	0.03
	WS4	6.91	0.51	...	...	...	0.011	0.01
	WS5	7.01	1.06	...	...	...	0.012	0.03
	WS6	7.30	2.28	...	...	...	0.009	0.02
	WS7	8.71	0.68	...	...	...	0.012	0.01
	WS8	9.13	1.41	...	...	...	0.012	0.02
	WS9	8.92	2.79	...	...	...	0.013	0.03
SERIES II: High-purity base  Commercial- purity base	WZ1	7.34	2.23	...	...	...	0.01	0.01
	WZ2	7.31	2.38	0.29	...	...	0.01	0.015
	WZ3	7.41	2.23	1.13	...	...	...	...
	WZ4	7.13	2.17	...	0.28	...	0.015	0.02
	WZ5	7.15	2.06	...	...	0.23	0.02	0.05
	WZ6	6.81	2.03	...	...	...	0.14	0.11
	WZ7	7.12	2.01	0.35	...	...	0.12	0.13
	WZ8	7.22	2.07	1.27	...	...	0.22	0.17
	WZ9	6.81	1.90	...	0.28	...	0.12	0.15
	WZ10	6.91	2.04	...	...	0.27	0.34	0.10
SERIES III: High-purity base  Commercial- purity base	XWA	7.27	2.37	1.38	...	0.29	0.005	0.03
	XWB	7.04	2.33	1.32	...	0.27	...	...
	XWC	7.05	2.30	1.40	0.28	0.26	0.02	0.04
	XWD	7.25	2.40	1.32	...	0.29	0.17	0.14
	XWE	7.21	2.35	1.37	0.28	...	...	...
	XWF	7.30	2.31	1.38	0.27	0.27	...	...

definitely within the ( $\alpha + T$ ) and three within the ( $\alpha + M$ ) phase field. Because of uncertainty regarding the occurrence of the  $\text{MgZn}_5$  or  $Z$  phase, three further alloys were selected to fall within the field which Mon-

The mechanical properties of the ternary alloys are shown in Table II, in which the mode of failure in tension is also indicated. Table III records the mechanical properties of the complex alloys and includes data on their behaviour in standard accelerated corrosion tests carried out in the unstressed condition.

Stress-corrosion tests were carried out at specific percentages of the proof stress, using the apparatus described in the Appendix (p. 169) and illustrated in Figs. 22–25 (Plates XXXI and XXXII). Average results for three specific fractions of proof stress are shown in Table IV. Stress/time-to-failure curves are plotted in Figs. 2–5 so that the stress-bearing properties of each alloy can be directly appraised.

For alloys of Series III an assessment was made (Table V) of the effect of applied stress on corrosion, by comparing the tensile-stress values of test-pieces which survived the full 100-day period of stress-corrosion testing with those of duplicate unstressed test-pieces exposed to the same environment.

Microsections, Figs. 6–21 (Plates XXIX and XXX), show typical structures and the mode of failure under stress-corrosion, as well as examples of the effect of corrosion on unstressed specimens.

## IV.—EXPERIMENTAL PROCEDURE

### 1. PREPARATION OF ALLOYS

The alloys were made in the laboratory from high-purity or commercial raw material, as appropriate, and special high-purity temper alloys. The constituents were melted in a plumbago pot coated with an alumina wash to prevent contamination, and the melt was de-

gassed with chlorine and poured by the Durville method. After cutting off the gate ends, the ingots measured  $8 \times 4 \times 1\frac{3}{4}$  in. in the case of the ternary alloys of Series I, and  $15 \times 8 \times 1\frac{3}{4}$  in. in the remaining alloys of Series II and III. They were homogenized at  $460^\circ\text{C}$ . for 24 hr., and the temperature reduced to  $440^\circ\text{--}420^\circ\text{C}$ . for hot rolling. Many of the alloys made from high-purity aluminium cracked to some degree in the early passes. Rolling was, where necessary, interrupted at  $\frac{3}{8}$  or  $\frac{1}{2}$  in. in order to machine out cracks, and was resumed after reheating, all strips being eventually brought to a thickness of between 0.3 and 0.25 in. by hot rolling. The strips were then cut into blanks, pickled in caustic soda to remove the hot-rolled surface, and cold rolled, with an intermediate anneal at 0.1 in., to the final thickness of 0.050 in., at which tensile and stress-corrosion testing were to be carried out.

## 2. HEAT-TREATMENT

In order to obtain a true measure of the effect on properties of varying the composition, a common temperature of  $460^\circ\text{C}$ . was employed for solution-treatment,

between room temperature and  $100^\circ\text{C}$ . have been shown to be particularly unfavourable to corrosion and stress-corrosion behaviour. Hansen<sup>5</sup> quotes  $125^\circ\text{C}$ . as the minimum ageing temperature, while Dix<sup>13</sup> employed  $121^\circ\text{C}$ . ( $250^\circ\text{F}$ .). More recently, Meikle<sup>21</sup> has indicated that even higher temperatures of ageing are desirable to improve atmospheric stress-corrosion characteristics.

## V.—MECHANICAL PROPERTIES

Mechanical properties were determined in triplicate on all alloys in both room-temperature-aged and artificially-aged conditions, and mean values are recorded in Table II for the ternary and in Table III for the complex alloys.

In the ternary alloys hardness increases progressively with increase in both zinc and magnesium contents, artificial ageing producing a higher hardness than room-temperature ageing, except in WS1. However, tensile strength values do not show the expected increments in the more highly alloyed members of the series, because of

TABLE II.—*Mechanical Properties of Ternary Alloys and Mode of Failure in Tensile Test.*

Alloy Series I	Nominal Additions		Aged for 3 Weeks at Room Temperature					Aged for 18 Hr. at $125^\circ\text{C}$ .				
			Hardness, D.P.N.	0.1% Proof Stress, tons/in. <sup>2</sup>	Tensile Strength, tons/in. <sup>2</sup>	Elongation, % on 2 in.	Type of Fracture	Hardness, D.P.N.	0.1% Proof Stress, tons/in. <sup>2</sup>	Tensile Strength, tons/in. <sup>2</sup>	Elongation, % on 2 in.	Type of Fracture
	Zn, %	Mg, %										
WS1	5	0.4	61	5.4	11.6	17	Transcrystalline	42	6.4	7.8	15	Transcrystalline
WS2	5	0.8	86	8.3	16.0	18	"	95	13.1	17.2	12	"
WS3	5	1.6	100	10.3	17.3	20	Partly intercrystalline	122	19.1	22.1	10	"
WS4	7	0.5	95	10.2	16.8	9	Mainly intercrystalline	103	14.9	19.2	13	Partly intercrystalline
WS5	7	1.0	113	12.8	16.9	6	"	138	22.7	24.7	3	Mainly intercrystalline
WS6	7	2.25	136	14.6	16.2	3	Intercrystalline	177	29.7	29.9	1	Intercrystalline
WS7	9	0.7	113	13.0	14.8	3	Intercrystalline	123	18.7	21.8	7	Mainly intercrystalline
WS8	9	1.4	137	12.9	15.1	2	"	169	...	21.6	...	Intercrystalline
WS9	9	2.8	158	...	14.5	...	"	197	...	13.5	...	"

this choice being governed by the presence of low-melting constituents in the more-complex alloys. Solution-treatment was carried out on machined test-pieces, with an immersion period of 30 min. in a salt-bath following by quenching in cold water.

The room-temperature age-hardening characteristics of the ternary alloys of Series I are perhaps worthy of comment. For eight of the alloys, i.e. excluding WS1, hardness plotted against log period-of-ageing resulted in a series of parallel curves, indicating a common mechanism of hardening.

All the alloys continued to age-harden at room temperature over prolonged periods of storage, but for the purpose of mechanical testing a standard period of 3 weeks was adopted, hardening and strengthening being then substantially complete.

Artificial ageing was carried out after an interval of at least one week after quenching, a precaution found to be necessary to obtain maximum strength in the milder ternary alloys. The period of ageing was 18 hr. at  $125^\circ\text{C}$ ., any higher temperature resulting in reduced tensile strength, while lower temperatures led to reduced corrosion-resistance. This is in general agreement with earlier work, in which ageing temperatures intermediate

premature intercrystalline brittle fracture. This brittle fracture occurs at a somewhat lower total alloy content than that quoted by Hérenghuel and Lacombe,<sup>3</sup> i.e. at 7% in the room-temperature-aged condition or 8% in the artificially-aged condition.

Large grain-sizes, in the range 0.1–0.5 mm. grain dia., were general with all the alloys of Series I, but values were not sufficiently consistent to record. Microstructures with a similar order of grain-size have been reproduced by Hérenghuel.

Of the complex alloys (Table III) based on the 7% zinc +  $2\frac{1}{4}\%$  magnesium alloy, only WZ4, made from a high-purity base with the addition of 0.25% manganese, fractured prematurely and then only in the room-temperature-aged condition. Premature intercrystalline fracture is not specifically associated with large grain-size, for grain diameters comparable with those in Series I were observed in WZ2 and WZ3, both of which gave elongations consistently exceeding 10% in the room-temperature-aged condition.

In Series II alloys the use of commercial-purity metal resulted generally in a finer grain-size and improved mechanical properties. However, in Series III there was no corresponding effect, and indeed differences in



mechanical properties associated with composition were small.

## VI.—STRESS-CORROSION PROPERTIES

### 1. TESTING CONDITIONS

The conditions were standardized at a temperature of 30° C., with a humidity of 85%. Testing was continuous, and spraying with a 3% solution of sodium chloride was carried out three times daily on the gauge-length of the stressed specimens and of duplicate unstressed specimens hung within the cabinet from small hooks screwed into the underside of the teak lid. Stress levels were selected

### 2. TIME TO FAILURE UNDER STRESS

The high-purity ternary alloys (Series I), apart from WS1, all fail in a short time under stress, life at any particular stress level falling progressively with increase in alloy content. The artificially-aged alloys sustain percentages of their respective proof-stress values somewhat higher than do the room-temperature-aged alloys.

In the quaternary alloys of Series II, manganese is almost without effect on time to failure, but copper and chromium both result in enhanced stress life. A much greater improvement in stress-corrosion properties is brought about in alloys of Series III by adding copper together with chromium. Alloys containing chromium

TABLE III.—Grain-Size, Mechanical Properties, and Loss of Strength in Accelerated Corrosion of Complex Alloys.

Alloy		Nominal Additions			Grain-Size, mm.	Aged for 3 Weeks at Room Temperature					Aged for 18 Hr. at 125° C.				
						Mechanical Properties Uncorroded			After 5 days in Salt-Peroxide Solution		Mechanical Properties Uncorroded			After 5 days in Salt-Peroxide Solution	
		Cu, %	Mn, %	Cr, %		0.1% Proof Stress, tons/in. <sup>2</sup>	Tensile Strength, tons/in. <sup>2</sup>	Elong., % on 2 in.	Reduction in Tensile Strength, %	Type of Attack	0.1% Proof Stress, tons/in. <sup>2</sup>	Tensile Strength, tons/in. <sup>2</sup>	Elong., % on 2 in.	Reduction in Tensile Strength, %	Type of Attack
SERIES II:															
High-purity base	WZ1	...	...	...	0.25	17.6	21.2	3	100	Pitting and severe localized intercrystalline	29.1	30.2	...	96	Pitting and severe localized intercrystalline
	WZ2	0.25	...	...	0.15	16.8	25.2	14	37	Pitting and localized intercrystalline	30.1	31.4	...	91	" "
	WZ3	1.25	...	...	0.15	20.1	30.2	13	44	Severe pitting	31.6	36.5	3	12	Pitting
	WZ4	...	0.25	...	0.04	17.9	19.8	2	20	Pitting and localized intercrystalline	30.6	34.4	...	8	"
Commercial-purity base	WZ5	...	...	0.25	0.03	19.4	29.6	11	Nil	Slight pitting	31.8	34.5	5	Nil	Slight pitting
	WZ6	...	...	...	0.05	17.3	28.1	20	26	Localized intercrystalline	29.8	33.2	6	Nil	Slight pitting
	WZ7	0.25	...	...	0.05	17.7	28.4	19	13	Pitting	29.8	33.8	8	Nil	Slight roughening
	WZ8	1.25	...	...	0.06	20.0	31.4	21	11	"	30.5	36.9	11	1	" "
	WZ9	...	0.25	...	0.015	18.8	29.4	18	10	Pitting and slight intercrystalline	29.8	33.8	8	Nil	Pitting
	WZ10	...	...	0.25	0.01	20.4	30.8	20	14	Pitting	32.0	35.1	8	4	"
SERIES III:															
High-purity base	XWA	1.25	...	0.25	0.03	23.2	35.8	21	9	Pitting and exfoliation	32.9	37.8	13	3	Severe localized pitting
	XWB	1.25	0.25	...	0.025	22.2	33.7	23	33	Severe pitting and exfoliation	32.0	37.8	14	8	" " "
	XWC	1.25	0.25	0.25	0.045	23.1	35.9	19	19	Pitting and exfoliation	33.3	38.5	15	2	Slight pitting
Commercial-purity base	XWD	1.25	...	0.25	0.025	23.5	35.4	20	10	Severe localized pitting and exfoliation	32.9	38.0	14	6	Slight pitting
	XWE	1.25	0.25	...	0.025	22.6	33.7	20	24	Severe pitting and exfoliation	32.2	38.0	13	10	Pitting
	XWF	1.25	0.25	0.25	0.030	22.9	36.0	21	21	Severe localized pitting and exfoliation	32.8	38.2	14	4	Slight pitting

at definite percentages of the proof stress, ranging between 10 and 90%.

Generally for each alloy and condition of heat-treatment at least ten stress-corrosion tests were made within this range, not including duplicate tests. Reproducibility is indicated by a statistical analysis of duplicate tests carried out on Series II alloys, in which for a total of 40 pairs of results the coefficient of variation has a mean value of 34%. Results expressed in terms of proof stress are quoted at three specific stress levels: 25, 50, and 90% of proof stress (Table IV). The plotted curves of stress against time to failure (Figs. 2-5) also indicate the high standard of reproducibility, most of the plotted points being either single or the mean of two (or more rarely three) values.

alone withstand 25% of their proof stress, while those containing both elements either withstand or only just fail to withstand the 100-day test at 50% of their proof stress in both the room-temperature-aged and artificially-aged conditions.

Stress/time curves plotted in Figs. 2-5 relate only to quaternary and more complex alloys of Series II and III. The plot is of actual applied stress, and the intention is to show the more practical implication of the results, rather than their theoretical significance, for which the percentage of the proof stress is appropriate.

There are relatively small differences between the curves for alloys made from high-purity and their opposite numbers made from commercial-purity metal. After room-temperature ageing (Figs. 2 and 4) the latter, on

the whole, withstand slightly higher stress. After artificial ageing (Figs. 3 and 5) the difference is even smaller, and, if anything, superior properties are found in the high-purity alloys.

All curves show initially a steep fall and thereafter, except in some of the room-temperature-aged alloys of Series III, a tendency to flatten out parallel with the time axis. The plotted points indicated by arrows (on the usual notation) represent the highest stress sustained for

bility to intercrystalline attack. In this test the high-purity ternary alloy is almost completely penetrated at the grain boundaries in both conditions of heat-treatment. Additions of copper and manganese substantially reduce the degree of attack in the high-purity series, while chromium has such a powerful inhibiting effect that attack is inappreciable, as is shown by the unchanged mechanical properties. Change to a commercial-purity base markedly reduces corrosion in the ternary alloy,

TABLE IV.—Stress-Corrosion Properties under Direct Tensile Loading over 100 Days.

Alloy		Nominal Additions			Aged for 3 Weeks at Room Temperature				Aged for 18 Hr. at 125° C.			
					Proof Stress, tons/in. <sup>2</sup>	Percentage of Proof Stress Applied and Time to Failure, hr.			Proof Stress, tons/in. <sup>2</sup>	Percentage of Proof Stress Applied and Time to Failure, hr.		
		Zn, %	Mg, %			25%	50%	90%		25%	50%	90%
SERIES I : High-purity base	WS1	5.0	0.4		5.4	1056	336	252	6.4	...	N.B.	N.B.
	WS2	5.0	0.8		8.3	264	19	22	13.1	...	264	22
	WS3	5.0	1.6		10.3	50	11	4	19.1	...	144	13
	WS4	7.0	0.5		10.2	2.25	1.5	0.2	14.9	...	3.75	0.75
	WS5	7.0	1.0		12.8	1.25	0.3	0.1	22.7	...	0.75	0.75
	WS6	7.0	2.25		...	...	...	...	29.7	...	0.75	0.6
	WS7	9.0	0.7		...	...	...	...	18.7	...	0.5	0.2
SERIES II :  High-purity base  Commercial-purity base		Cu, %	Mn, %	Cr, %								
	WZ1	...	...	...	17.6	1.0	0.05	F.D.L.	29.1	2.1	0.9	F.D.L.
	WZ2	0.25	...	...	16.8	2.2	1.3	0.3	30.1	26	...	2.5
	WZ3	1.25	...	...	20.1	8.7	1.8	0.8	31.6	9	3.2	F.D.L.
	WZ4	...	0.25	...	17.9	0.3	0.1	F.D.L.	30.6	...	F.D.L.	F.D.L.
	WZ5	...	...	0.25	19.4	N.B.	27	1.1	31.8	640	35	4.5
	WZ6	...	...	...	17.3	4	1.8	0.8	29.8	3	1.9	0.9
	WZ7	0.25	...	...	17.7	5	2.0	1.2	29.8	13	7	3.0
	WZ8	1.25	...	...	20.0	33	3.3	1.0	30.5	...	...	3.4
	WZ9	...	0.25	...	18.8	3.2	1.0	0.6	29.8	4	...	1.5
	WZ10	...	...	0.25	20.4	N.B.	11.5	1.4	32.0	142	11	4
SERIES III :  High-purity base  Commercial-purity base	XWA	1.25	...	0.25	23.2	N.B.	418	12	32.9	N.B.	2130	56
	XWB	1.25	0.25	...	22.2	...	10	2	32.0	...	120	5.5
	XWC	1.25	0.25	0.25	23.1	N.B.	N.B.	N.B.	33.3	N.B.	2168	203
	XWD	1.25	...	0.25	23.5	N.B.	N.B.	152	32.9	...	1935	180
	XWE	1.25	0.25	...	22.6	...	290	1.8	32.2	...	17.5	1.7
	XWF	1.25	0.25	0.25	22.9	N.B.	N.B.	327	32.8	N.B.	N.B.	300

N.B. = not broken after 2400 hr.

F.D.L. = failed during loading.

2400 hr. without fracture. Lower stress values on other unbroken specimens are not shown. The indication is that in many of the alloys 2400 hours' testing is adequate to indicate the asymptotic trend, and to provide an approximate value of the maximum safe level of stressing for a particular alloy. This level is raised by alloying with copper, manganese, and chromium, as well as by artificial ageing, the highest level being approximately 20 tons/in.<sup>2</sup> in alloys XWC and XWF in the artificially-aged condition.

### 3. COMPARISON WITH UNSTRESSED CORROSION

The results of accelerated corrosion testing of unstressed specimens of Series II and III in a standard salt-peroxide medium are also shown in Table III. The method of accelerated testing has been described previously,<sup>20</sup> and its main value is in assessing suscepti-

especially in the artificially-aged condition, while the effect of further alloying additions is masked by the impurities in the aluminium itself. In Series III compositional differences have less effect on loss of strength and the purity of the aluminium base also appears to be of little consequence; furthermore, the four alloys containing chromium are not appreciably better in corrosion-resistance than the two alloys without chromium, while the artificially-aged are again notably superior to the room-temperature-aged materials.

Table V compares stressed and unstressed corrosion in alloys of Series III only. Column (ii) gives the reduction in tensile stress as a result of the 100 days' period of exposure under the stress recorded in column (i), the specimen being then unbroken. Column (iii) records similar data for unstressed test-pieces exposed for 100 days to the same conditions, i.e. suspended in the stress



cabinet, each beside a corresponding stressed specimen, and sprayed with sodium chloride solution at the same intervals. As a duplicate unstressed specimen was exposed in the cabinet during every stress test, the number of results in column (iii) is the same as in column (ii), although in (iii) there is no difference in the treatment of

artificially-aged specimens. In other words, there is a prolonged period of induction with no measurable deterioration in properties, but once stress-corrosion cracking begins it rapidly spreads and leads to the fracture of the specimen.

The 100-day unstressed exposure to neutral sodium

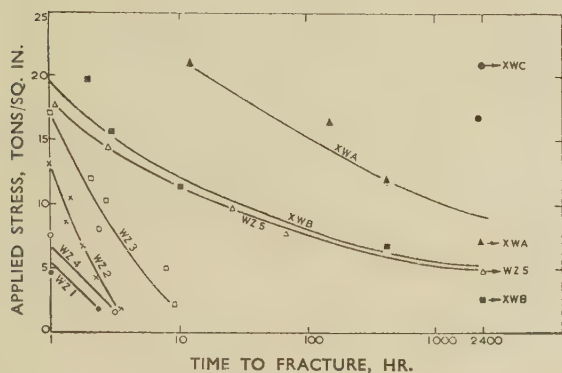


FIG. 2.—Aged at Room Temperature.

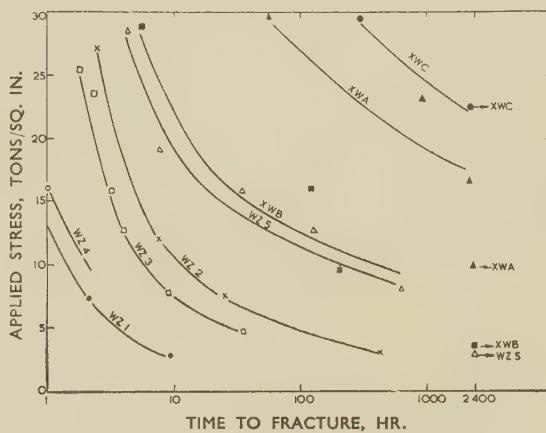


FIG. 3.—Aged at 125° C.

FIGS. 2 and 3.—Stress/Time Curves for Alloys Made with High-Purity Base.

KEY TO FIGS. 2 AND 3

● WZ1  
× WZ2  
□ WZ3

○ WZ4  
△ WZ5

▲ XWA  
■ XWB  
● XWC

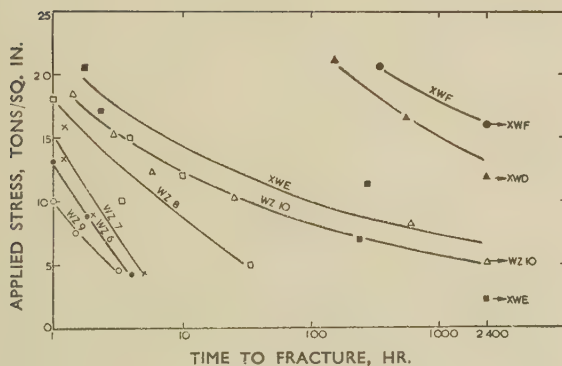


FIG. 4.—Aged at Room Temperature.

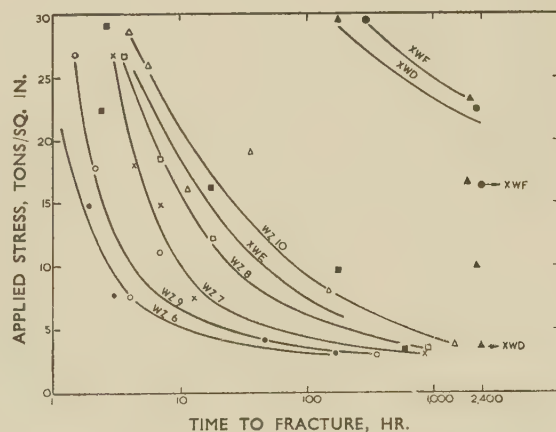


FIG. 5.—Aged at 125° C.

FIGS. 4 and 5.—Stress/Time Curves for Alloys Made with Commercial-Purity Base.

KEY TO FIGS. 4 AND 5

● WZ6  
× WZ7  
□ WZ8

○ WZ9  
△ WZ10

▲ XWD  
■ XWE  
● XWF

these duplicate specimens. Column (iv) quotes results, taken from Table III, of corrosion tests in the salt-peroxide medium.

It is evident from a comparison of values in columns (ii) and (iii) that the application of stress below that required to cause failure has led to no damage to the specimen over and above that suffered by a similar unstressed specimen. A similar conclusion must be drawn from a comparison of columns (vi) and (vii), relating to

chloride (column (iii)) reveals no marked trend in corrosion behaviour in respect of differences in composition, the two chromium-free alloys XWB and XWE suffering about the same degree of attack as the remaining four chromium-bearing alloys. This is in contrast with salt-peroxide tests in which (column (iv)) greater attack occurs in the chromium-free alloys. Both types of unstressed corrosion test cause much less attack on alloys aged artificially than on those aged naturally.

## 4. ASSOCIATED MICROSTRUCTURES

Microstructures of sections normal to sheet specimens in the direction of rolling are illustrated in Figs. 6-15 (Plate XXIX). On the left are alloys prepared from high-purity and on the right those prepared from commercial-purity aluminium. The copper addition has no effect on grain-size, but manganese produces a substantial refinement of grain in both series. Chromium has the effect of causing the grains to be elongated, although grain-size is about the same as with manganese. No appreciable further refinement of structure occurs when copper and manganese are present in addition to chromium, but the elongated type of grain is somewhat more pronounced. Commercial-purity alloys are in general of rather finer grain-size than the corresponding high-purity alloys.

Typical transverse sections through fractured surfaces of test-pieces broken in the stress-corrosion apparatus

showing an alloy with copper and manganese and the latter one with copper, manganese, and chromium. The more indirect path of the corrosion crack as a result of the elongated grain structure in the chromium-bearing alloy is clearly apparent.

## VII.—DISCUSSION

Attempts to relate stress-corrosion behaviour to the phase field concerned, and thus to the nature of the precipitated phase, indicate that this factor has little significance. For example, comparison of times to failure at definite percentages of the proof stress in the ternary alloys (Table V) shows a greater difference between WS1 and WS2 in the same equilibrium phase field (Fig. 1) than between WS2 and WS3 in different phase fields, and in the same way WS5 is closer in behaviour to WS6 than to WS4.

TABLE V.—Comparison of Stressed and Unstressed Corrosion.

Alloy Series III	Aged for 3 Weeks at Room Temperature				Aged for 18 hr. at 125° C.			
	Stressed Corrosion		Unstressed Corrosion		Stressed Corrosion		Unstressed Corrosion	
	3% NaCl in Cabinet		3% NaCl in Cabinet	Salt-Peroxide Immersion	3% NaCl in Cabinet		3% NaCl in Cabinet	Salt-Peroxide Immersion
	Stress Applied, % Proof Stress	Reduction in T.S., % in 100 days	Reduction in T.S., % in 100 days	Reduction in T.S., % in 5 days	Stress Applied, % Proof Stress	Reduction in T.S., % in 100 days	Reduction in T.S., % in 100 days	Reduction in T.S., % in 5 days
XWA	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)
XWB	30	43	37	9	30	12	13	3
XWC	10	19	20	33	10	8	12	8
	50	32	35	} 19 {	30	13	13	} 2
	70	25	27		70	9	8	
	90	20	33					
XWD	30	17	18	10	10	21	25	6
	50	29	27					
XWE	10	21	22	24	...	...	...	10
XWF	50	23	26	} 21	50	9	9	4
	70	23	23					

are shown in Figs. 16 and 17 (Plate XXX). In the copper-bearing alloy WZ3, fracture is entirely intercrystalline, as it is in the ternary alloy WZ1. The manganese-bearing alloy WZ4, with its finer grain, fractures mainly in an intercrystalline manner, but there is some disruption of grains.

Examples of corrosion in the unstressed condition in salt-peroxide are illustrated in Figs. 18 and 19 (Plate XXX). Fig. 18 shows the high-purity ternary alloy WZ1 aged at room temperature, in which corrosion is intercrystalline, while Fig. 19 shows the effect of adding 1.25% copper (alloy WZ3), when attack occurs both at grain boundaries and at their centres, intermediate areas being less affected.

The observation of crack progression in a tensile test proved to be impossible, because specimens under tension showed little damage when removed from the stress frame shortly before the expected time of fracture. In order to study the early stages of cracking, specimens were stressed by bending, using neutral sodium chloride as the corroding medium. Examples of cracking are illustrated in Figs. 20 and 21 (Plate XXX), the former

The basic alloy containing 7% zinc and 2½% magnesium is improved by alloying, the iron and silicon introduced from the use of commercial-quality aluminium being themselves beneficial, while chromium, copper, and manganese all produce more definite increases in time to failure, thus confirming earlier work. In general, the room-temperature-aged and artificially-aged alloys show about the same resistance to stress-corrosion when both are stressed to the same ratios of their respective proof stresses, but the artificially-aged alloys, being of much higher proof and tensile stress, are capable of withstanding the greater actual stress.

One of the factors associated with the improvement in stress-bearing level brought about by alloying is refinement of grain-size. Thus, in the ternary alloys, the substitution of commercial-purity for high-purity base results in a reduction of grain-size from 0.25 mm. (Fig. 6, Plate XXIX) to 0.05 mm. (Fig. 11, Plate XXIX), while the stress withstood for a similar time to fracture is about doubled. Manganese (Figs. 8 and 13, Plate XXIX) and chromium (Figs. 9 and 14, Plate XXIX) both cause considerable further grain refinement, but while the manganese-



bearing alloys have equiaxed structures, the chromium-bearing alloys have elongated grains, with the length up to five times the width. This elongation of the grain structure in chromium-bearing alloys has been previously noted by Dix,<sup>13</sup> who regarded it as partly responsible for the improved stress-corrosion performance associated with the presence of chromium. It is perhaps significant in this connection that when manganese is added in the absence of chromium it has no effect on stress-corrosion properties, but when it is added to a chromium-bearing alloy it has a pronounced beneficial effect. In conformity with this, alloys containing both elements (Figs. 10 and 15, Plate XXIX) show an even more pronounced elongation of grain structure, with a width: length ratio of at least 10:1 in many of the grains. The effect of this elongated structure on crack propagation under stress will be evident from Figs. 20 and 21 (Plate XXX).

Copper alone added to the ternary alloy has a pronounced beneficial effect, and added in conjunction with manganese or chromium its value is enhanced. This cannot be explained on the basis of grain-size, because copper appears to have no grain-refining effect, as will be evident from Figs. 7 and 12 (Plate XXIX). However, as corrosion tests in salt-peroxide solution reveal, the ternary alloy (Fig. 18, Plate XXX) is attacked entirely on the grain boundaries, and because of the large grain-size, penetration is rapid. The copper-bearing alloy (Fig. 19, Plate XXX) suffers attack both at grain centres and at their boundaries, an intermediate area being unattacked. Although under stress-corrosion conditions all alloys fail by intercrystalline attack, it seems likely that in the presence of copper the difference in potential between the grain boundaries and various parts of the grains themselves is small, with the grain centres probably rather more anodic than the grain boundaries.

Dix<sup>13</sup> observed that chromium additions not only affected grain-size and shape, but also the nature of grain-boundary precipitation on ageing, and deduced that both these factors were probably significant. However, since he assessed susceptibility to stress-corrosion from statistical data on the number of specimens failing over 100 days, the choice of testing stress was the deciding factor, and by taking 75% of the yield stress the effect of chromium was exaggerated. The present comparison of safe stress levels, with or without chromium, indicates a difference which is reasonably accounted for by the difference in grain structure. Nevertheless, because grain structures are affected to a considerable extent by the method of fabrication, it is evident that the beneficial effects of chromium or other favourable alloying constituents cannot be expressed by a single parameter common to all wrought forms of alloys. However, chromium appears to create a strong tendency to a fibrous elongated structure in both rolled and extruded products, and its influence on stress-corrosion is therefore generally beneficial.

#### ACKNOWLEDGEMENTS

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Automotive Products, Ltd, Leamington Spa, for invaluable advice on dash-pot design.

## APPENDIX

### STRESS-CORROSION TESTING APPARATUS

Spring loading was selected as the only possible means of obtaining direct-tension equipment of sufficiently compact design. With a maximum load requirement of 3000 lb., the most serious design problem was to find means of dissipating the considerable energy of a compressed spring released by the fracture of the specimen, without causing damage to the equipment or interference with neighbouring specimens. This problem was solved by fitting each stress unit with an oil-filled dash-pot to control the release of energy, a device which was the key to the successful operation of the installation of 24 stress units illustrated in Fig. 22 (Plate XXXI). Its reliability may be deduced from the performance of the installation over a period of five years, in the course of which neither damage nor interference of any kind has been caused by breaking specimens.

The stress unit, illustrated in Fig. 23 (Plate XXXII) is constructed on a rigid aluminium alloy frame (1) sand-cast in D.T.D. 424, anodized and stove-enamelled to provide the maximum protection against the corrosive spray to which this component is subjected. A heavy coil spring (2), cadmium-plated as protection against corrosion, rests on the machined upper face of the casting, and is surmounted by a cap (3), machined from wrought high-strength aluminium alloy, from which the specimen is supported via twin aluminium alloy stress bars free to swivel on  $\frac{1}{2}$ -in. pins of hardened steel at both their upper and lower ends. At the lower end of the specimen, shorter stress bars are similarly attached to an aluminium head (4) integral with a 1-in.-dia. screw passing through a slot in the cast frame, and terminating in a nut (5) with peripheral holes for capstan tightening. Integral with the frame are lugs for lifting purposes (6) and a flange (7) from which the unit is supported during the stress-corrosion tests, when it rests on a sponge-rubber pad (8). The stress bars, as well as the cast body, are anodized and stove-enamelled as protection against corrosion, while the lower threaded stress-member (4) is anodized only. Other aluminium components have a natural finish.

The dash-pot (9) is mounted on pillars bolted to the cap (3). It is machined entirely from aluminium alloy components, with the exception of the plunger (10), which is a steel rod passing right through the assembly and integral with a steel piston, 0.003 in. smaller in dia. than the aluminium cylinder in which it operates. The downward movement of the plunger is unopposed, the light mineral oil with which the pot is filled flowing from the lower to the upper end of the cylinder via a by-pass channel with spring-loaded ball valve. In the reverse direction movement can occur only by the escape of oil between the piston and cylinder walls. Correctly designed Neoprene sealing rings allow movement of the plunger with negligible friction and without leakage of oil over long periods of use.

To load the stress unit, the nut (5) is slackened off, the tensile test-piece secured in position with steel pins and wing nuts, and the calculated stress applied in an Amsler tensile-testing machine. For this purpose the unit is

supported from the flange (8) on a special cradle, as shown in Fig. 24 (Plate XXXII). With the supporting cradle and unit hanging freely, the testing machine is adjusted to zero reading, and connection is then made to the lower cross-head with the adaptor nut (11). After the desired load has been applied, the nut (5) is tightened and the unit is then removed from the tensile machine. The dash-pot plunger is finally pushed down into contact with the spring cap, and the nut (11) removed.

When the spring is utilized over its optimum range of compression, small relaxations have a negligible effect on the load. To cover the range of loads involved, it was necessary to have springs of three sizes. These are of identical length and diameter but differ in gauge, and are capable of applying maximum loads of 750, 1500, and 3000 lb., respectively. The springs are easily changed after taking off the dash-pot unit, which involves only the removal of two nuts.

In order to check the effect of stretch or relaxation, either in the apparatus or the specimen, during setting up as well as during the period of stress-corrosion testing, provision was made for the fitting of a dial gauge between the cast body and the spring cap, as shown in Fig. 25 (Plate XXXII). As soon as loading was complete, and before removal from the tensile machine, the dial gauge was set to zero. Relaxation on removing from the testing machine was thereby measured and could be compensated for by adjusting the capstan nut. However, this effect on the loading proved to be negligible with a suitable choice of spring, although in experiments the gauge was retained throughout the stress-corrosion period. While the specimen remained unbroken it was thus possible to measure the total relaxation and to estimate its effect on the applied load. In a series of such experiments the load after 100 days' testing was shown to be normally within  $\pm 1\%$  of the starting load, with a maximum variation of  $\pm 3\%$ . Dial gauges were not therefore employed in the general programme of testing.

The cabinets, illustrated in Fig. 22 (Plate XXXI), are of double-walled welded aluminium sheet construction. The lid, of heavy teak, has eight rectangular holes from which the stress units are supported. Smaller holes take thermometer and hygrometer stems. The sides and base of the cabinet are welded, and sealing around the periphery of the lid and at the various openings is effected by sponge-rubber gaskets.

Free space at the ends and in the base accommodates the thermostat and the humidifying device. A constant temperature is maintained by a bimetallic element operating a 100-V. bulb shielded by a baffle, with a small electric fan mounted in the front wall. A constant humidity of 85% is achieved by placing a flat dish containing a saturated solution of potassium chloride in the base of the cabinet. A specially constructed atomizer sprays both sides of the specimen simultaneously, hinged windows being provided for this purpose, as shown in the left-hand cabinet of Fig. 22.

In the absence of visible or audible indication of fracture, recording devices are essential. For this purpose a full complement of hour-meters and neon warning lights are fitted to each cabinet. Each loaded stress unit, when placed in position, is fitted with a microswitch attached to the body of the dash-pot, with its trigger mechanism in contact with the head of the plunger, as shown in Fig. 25 (Plate XXXII). This, when plugged into the hour-meter circuit, starts the meter which records the life of the specimen. The tripping of the circuit when the specimen breaks stops the hour-meter and lights the warning neon light.

Perspex covers over the spring and dash-pot assemblies, shown in position in Fig. 22, are an important refinement. These not only keep the assemblies clean and free from dust, but they also improve the accuracy of temperature control, a 100-W. lamp bulb being installed for this purpose in parallel with the bulb in the inner cabinet. Without this device, conduction of heat away from the cabinet proper takes place through the stress units themselves, disturbing the thermostatic control and causing condensation on the upper ends of the stressed specimens.

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### SYNOPSIS

The zone-refining process has been applied to copper containing known amounts of various other elements and the segregation of the impurities followed by spectrographic analysis. From the results of preliminary experiments, a rate of zone travel of 11 mm./hr. was selected for a detailed investigation of the segregation produced during the zone-refining of an alloy containing 0.01 wt.-% of the elements antimony, chromium, cobalt, iron, manganese, nickel, silicon, silver, and tin. All the added elements segregated in the direction of travel of the molten zone, with the exception of iron, cobalt, and nickel, which segregated in the reverse direction.

The experimental results were used, together with a mathematical expression based upon certain assumptions, to calculate effective partition coefficients for the various impurity elements. A comparison of these values with corresponding values estimated from published phase diagrams showed them to be in approximate agreement, although the amount of segregation was usually less than would have been expected. This showed that the theoretical assumptions upon which the mathematical analysis had been based were not completely fulfilled in these experiments. The assumptions most likely not to be fulfilled are those of homogeneous composition in the liquid phase and equilibrium at the freezing interface.

## I.—INTRODUCTION

IN recent years a technique known as zone-refining has been developed for the preparation of material in a high state of purity. The process consists essentially of segregating the impurities to one or other end of a bar of the material by slowly passing along its length a narrow molten zone. The operation is repeated a number of times, and during each pass the amount of segregation increases until, if sufficient passes are employed, a state of equilibrium is reached. The amount of segregation to be expected under given conditions has been studied theoretically by a number of workers,<sup>1-3</sup> and the technique is used in the manufacture of pure materials for semi-conductor devices.

Only a limited amount of information has so far been published relating to the zone-refining of the more familiar metals, and in the present paper the segregation of impurities during the zone-refining of impure copper is described. Specific impurity elements have been added to copper in sufficient quantity for their segregation to be followed by spectrographic analysis, and the results have been used to calculate effective partition coefficients.

## II.—EXPERIMENTAL

### 1. PREPARATION OF ALLOYS

Two dilute copper alloys of known composition were prepared by adding small quantities of specified elements to oxygen-free high-conductivity copper (99.99%). The major impurities were sulphur 0.003, silver 0.003, and nickel 0.0007%, and all the added alloying elements contained less than 0.5% of total impurity. The

melting was carried out in a magnesia crucible under an atmosphere of purified hydrogen, using high-frequency heating. Initially, concentrated alloys were made by melting the copper with weighed quantities of the required elements. These master alloys were diluted by remelting with additional quantities of copper to obtain alloys of the following composition:

Alloy A: Chromium, cobalt, iron, nickel, and silver, each at a concentration of 0.05%, balance copper.

Alloy B: Antimony, chromium, cobalt, iron, manganese, nickel, silicon, silver, and tin, each at a concentration of 0.01%, balance copper.

The copper alloy ingots were cold rolled to bar 9 mm. square and cut into 20-cm. lengths. The surfaces of these bars were cleaned first mechanically and then chemically, with 60% nitric acid. A portion was removed from the end of each bar for spectrographic analysis.

### 2. APPARATUS

A high-purity graphite boat, degassed at about 2800°C. in a graphite resistor furnace before use, was of dimensions such that the 20-cm.-long copper bar fitted closely inside it. The boat containing the sample to be treated was placed inside a transparent silica tube (25 mm. in dia.), through which passed purified and dried hydrogen (Fig. 1). To one end of the graphite boat was attached a silica rod which slid freely through a rubber bung sealing one end of the silica tube. A slight positive pressure of hydrogen was maintained inside the apparatus to prevent air entering at the junction of the rubber bung and the silica rod and thus contaminating the atmosphere. The rod was connected to a drive mechanism which pulled the graphite boat at a controlled speed along the silica tube. The speed of travel

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of the boat could be altered by changing the reduction gears connecting the drive mechanism to a constant-speed motor. By observing the movement of the end of the boat with a travelling microscope, it was shown that the speed of travel could be maintained constant and uniform over long periods of time.

The copper bar was heated at one point along its length by means of a single turn of a copper coil joined to a 25-kW. high-frequency unit. Although most of the energy input was due to coupling between the high-frequency coil and the graphite boat, a well-defined molten zone of copper was obtained which had its solid/liquid interfaces approximately at right-angles to the axis of the bar.

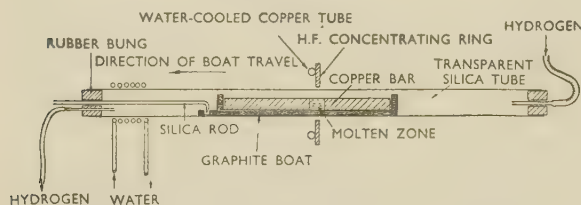


FIG. 1.—Apparatus for the Zone-Refining of Copper.

Owing to the high thermal conductivity of copper, the heat loss along the bar was considerable; this meant that when the molten zone was near one end of the bar less power was required than when the zone was near the centre. It was possible, however, to maintain a zone length of  $2.2 \text{ cm.} \pm 10\%$  by varying the power input as the position of the zone altered. The ratio zone length : bar length was therefore approximately 0.1.

### 3. PROCEDURE

The graphite boat containing the specimen to be refined was placed in such a position that a molten zone was formed at one end of the bar, and the boat was pulled through the coil at a controlled speed until one pass had been completed. The boat was then returned to its original position and the process repeated as required. After treatment, small samples were cut from the bar for spectrographic examination; chemical cleaning was carried out before analysis to remove any possible surface contamination.

In order to confirm that contamination was not taking place from the graphite boat or during sectioning, a preliminary zone-refining experiment was carried out with a bar of unalloyed copper. Samples from each end of this bar were analysed after one pass of the molten zone and the results compared with similar results on untreated material.

A series of three experiments was carried out with alloy A to determine the rate of travel of the zone to be employed in later experiments. Three separate bars were refined at speeds of 5, 11, and 13 mm./hr., respectively, each bar being subjected to three passes of the molten zone. After treatment, slices were cut for spectrographic analysis from the ends and the centre of each bar. The segregation of impurities at a suitable speed was investigated in more detail on alloy B, and in order to follow the rate of purification with respect to the number of passes, small samples were removed from a point 2.5 cm. from the starting end after every third pass. After nine and eighteen passes, samples for analysis were

removed from eight different positions along the length of the bar.

All the analytical results presented in the paper are based on spectrographic measurements obtained by the molten-globule technique.<sup>4</sup> As will be discussed later, the percentages given have more significance as relative than as absolute values.

### 4. RESULTS

The control experiment with unalloyed copper had shown that no contamination occurred during one pass of the molten zone; the distribution of iron was apparently unchanged, as would be expected from later results, and the silver was showing signs of segregating (Table I).

TABLE I.—Analysis of Unalloyed Copper Bars.

Sample	Iron, %	Lead, %	Silver, %	Tin, %
Before treatment	0.0003	0.001	0.003	0.0005
Starting end; one pass	0.0003	N.D.	0.001	N.D.
Finishing end; one pass	0.0003	„	0.003	„

The results obtained after refining three separate bars at speeds of 13, 11, and 5 mm./hr. showed that the slowest speed was not necessary (Table II). After three passes

TABLE II.—The Effect of Rate of Zone Travel.

Sample	Rate of Zone Travel, mm./hr.	Chromium, %	Cobalt, %	Iron, %	Nickel, %	Silver, %
Before treatment	...	0.05	0.05	0.05	0.05	0.05
Starting end	13	0.05	0.05	0.05	0.05	0.02
Centre		0.05	0.05	0.05	0.05	0.05
Finishing end		0.05	0.05	0.05	0.05	0.10
Starting end	11	0.02	0.05	0.05	0.05	0.02
Centre		0.02	0.05	0.05	0.05	0.05
Finishing end		0.15	0.05	0.05	0.05	0.10
Starting end	5	0.02	0.05	0.05	0.05	0.03
Centre		0.05	0.05	0.05	0.05	0.05
Finishing end		0.10	0.05	0.05	0.05	0.07

no segregation of iron, cobalt, or nickel was apparent at any of the speeds, but the lack of segregation was to be expected, since, as shown later, these elements segregate to the starting end of the bar. However, the results for silver and chromium showed that as regards these elements the intermediate speed of 11 mm./hr. was as effective as the slower speed. The intermediate speed was therefore adopted for subsequent experiments.

The remaining experimental results reported were all obtained using one bar of alloy B, which was refined at a speed of 11 mm./hr. The data contained in Table III show the variation of concentration with respect to the number of passes, at a distance 2.5 cm. from the starting end.

All the added elements except iron, cobalt, and nickel segregated to the finishing end of the bar, the segregation increasing as the number of passes increased. The efficient segregation of antimony and tin was apparent from their removal to a level below that detectable by spectrographic analysis after only three passes of the molten zone.



The results of spectrographic analysis on samples taken from various positions along the bar after nine and eighteen passes are given in Tables IV and V, respectively. When graphs were plotted from the results recorded in these tables to show concentration of added element against distance along the bar, smooth curves were obtained. Assuming no loss of a given solute element

spectrographic data were not sufficient for the drawing of distribution curves for these elements.

The corrected curves for the various elements after nine and eighteen passes are shown in Figs. 2 and 3, respectively, and Fig. 4 gives the corresponding total amount of solute. A considerable movement of the alloying elements has taken place after nine passes, and

TABLE III.—*The Effect of the Number of Passes.*

Pass Number	Antimony, %	Chromium, %	Cobalt, %	Iron, %	Manganese, %	Nickel, %	Silicon, %	Silver, %	Tin, %
Before treatment	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
3	N.D.	0.003	0.01	0.01	0.01	0.01	0.008	0.005	N.D.
6	"	0.001	0.01	0.01	0.004	0.01	0.005	0.002	"
9	"	0.001	0.01	0.01	0.002	0.01	0.002	0.0005	"
12	"	0.001	0.01	0.01	0.0005	0.06	0.002	N.D.	"
15	"	0.0003	0.01	0.03	N.D.	0.06	N.D.	"	"
18	"	0.0001	0.006	0.01	"	0.06	"	"	"

N.D. = not detected.

TABLE IV.—*Variation in Composition Along the Bar After Nine Passes.*

Distance from Starting End, mm.	Antimony %	Chromium, %	Cobalt, %	Iron, %	Manganese, %	Nickel, %	Silicon, %	Silver, %	Tin, %
13	N.D.	0.001	0.03	0.03	0.001	0.06	0.002	0.0005	N.D.
55	"	0.003	0.02	0.005	0.005	0.03	0.005	0.0001	"
81	"	0.005	0.015	0.005	0.015	0.02	0.008	0.002	"
103	"	0.01	0.01	0.003	0.015	0.01	0.01	0.003	"
133	"	0.01	0.008	0.002	0.03	0.01	0.03	0.005	0.0005
159	"	0.02	0.006	0.001	0.03	0.007	0.04	0.01	0.0003
182	0.1	0.1	0.003	0.001	0.05	0.003	0.1	0.02	0.01
187	0.1	0.1	0.003	0.001	0.05	0.002	0.1	0.03	0.01
Correction factors used in preparing Figs. 2, 3, and 4 from these data	...	0.78	0.70	1.30	0.53	0.45	0.42	2.2	...

TABLE V.—*Variation in Composition Along the Bar After Eighteen Passes.*

Distance from Starting End, mm.	Antimony, %	Chromium, %	Cobalt, %	Iron, %	Manganese, %	Nickel, %	Silicon, %	Silver, %	Tin, %
0	N.D.	0.0001	0.2	0.03	N.D.	0.1	N.D.	N.D.	N.D.
25	"	0.0001	0.06	0.01	"	0.06	"	"	"
50	"	0.0003	0.06	0.005	"	0.03	"	"	"
75	"	0.001	0.03	0.003	0.0005	0.01	0.005	"	"
100	"	0.001	0.02	0.002	0.001	0.002	0.005	0.001	"
125	"	0.01	0.01	0.001	0.015	0.001	0.008	0.005	"
150	0.0005	0.5	0.01	0.001	0.10	0.001	0.4	0.06	0.01

during the refining process, the area under the distribution curve for that element, representing the total amount of the element present, should be equal to the area under the initial concentration line. This, however, was not found to be the case. The discrepancy is believed to be due to the approximate nature of the spectrographic data and, therefore where necessary, the curves have been displaced so that the areas underneath are in agreement with the known amounts added. This displacement has been achieved by multiplying the results for a given element by an empirical factor (Table IV). Owing to the rapid segregation of antimony and tin, the

this movement has become more pronounced after eighteen passes. The degree of segregation for different elements varies and accumulation of solute at the finishing end is more pronounced than at the starting end. After eighteen passes about a quarter of the bar at the starting end was spectrographically free from antimony, silver, silicon, manganese, and tin, and a 12-cm. length in the centre of the bar had undergone a 70% decrease in total alloy content.

The direction of segregation of the various solute elements can be correlated with the corresponding phase diagrams. Iron, cobalt, and nickel are known to increase

the melting point of copper and, in accordance with this, segregation has taken place in the opposite direction to the travel of the molten zone; the elements segregating to the finishing end all reduce the melting point of copper. The degree of segregation of these elements varied con-

siderably; it was particularly efficient for antimony and tin, as might be expected from an examination of the appropriate phase diagrams.<sup>5</sup>

### III.—DISCUSSION

Although the individual experimental results for the amount of a given element present at a given position were only approximate, it was believed that the general shape of the curves obtained after nine passes of the molten zone could be used to calculate effective partition coefficients.

#### 1. AN EXPRESSION FOR THE PARTITION COEFFICIENT

A number of different mathematical treatments are possible,<sup>1-3</sup> leading to the same final expression; the treatment by Reiss<sup>2</sup> has been adopted here, since it conveys a clear physical understanding of the process.

Consider the zone-refining of a long metal bar of cross-sectional area  $A$  containing a single impurity element distributed uniformly throughout the otherwise pure metal at a concentration of  $C_0$ . Let it be assumed that ideal conditions for zone-refining prevail so that: (i) diffusion in the solid state is negligible, (ii) mixing in the liquid state is complete, (iii) the partition coefficient  $k$  is independent of composition ( $k$  = ratio solubility in solid : solubility in liquid, at a given temperature), and (iv) the rate of zone travel is sufficiently slow for equilibrium to be maintained at the freezing interface. If the length of the molten zone is  $L$  and  $C$  is the concentration of impurities in the solid at the freezing interface, then the concentration in the liquid zone will be  $C/k$  and the total impurity content  $\frac{ALC}{k}$ .

Let the concentration in the solid at any point  $x$  be  $C_n(x)$  after the  $n$ th pass, then before the zone front on the  $n$ th pass reaches a given point  $a$  the concentration at  $a$  will still be  $C_{n-1}(a)$ , and the amount of solute contained in the volume of bar between  $a$  and  $(a + L)$  will be :

$$A \int_a^{a+L} C_{n-1}(x) dx \quad (\text{see Fig. 5})$$

When the trailing interface of the zone reaches  $a$ , all the solute which is to move across  $a$  has done so, and the total amount of solute in the liquid zone is now :

$$\frac{AL}{k} C_n(a)$$

Thus, the flow of solute material across the interface at  $a$  due to the  $n$ th pass alone is given by :

$$Af_n(a) = \frac{AL}{k} C_n(a) - A \int_a^{a+L} C_{n-1}(x) dx \quad (1)$$

Here,  $f_n$  is a transport function containing the number of passes  $n$  as a variable. Generally, in transport processes involving time, we have the well-known continuity equation :

$$\frac{\partial f}{\partial a} = - \frac{\partial C}{\partial t} \quad \dots \quad (2)$$

where, in this case,  $C$  is a function of distance and time.

In the zone-melting problem, the time is replaced by

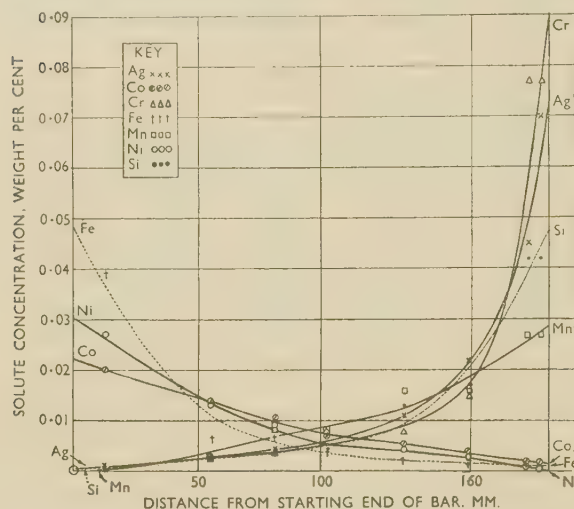


FIG. 2.—State of Segregation in the Bar of Alloy B After Nine Passes of the Molten Zone.

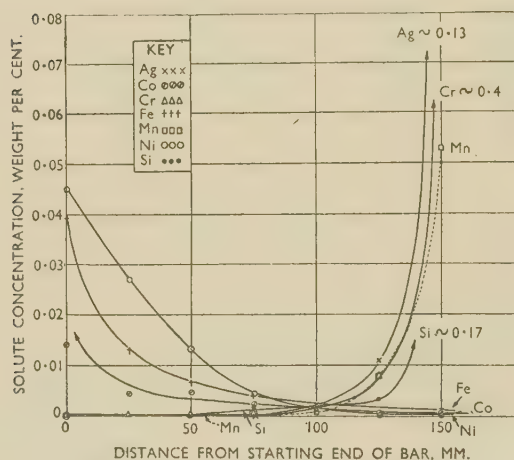


FIG. 3.—State of Segregation in the Bar of Alloy B After Eighteen Passes of the Molten Zone.

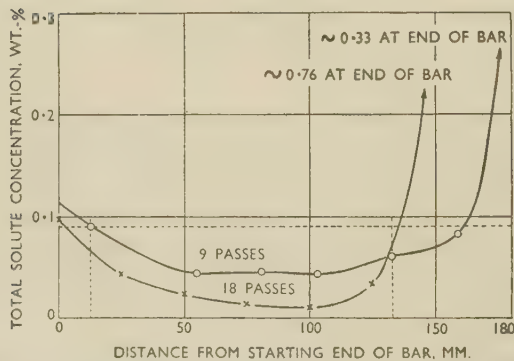


FIG. 4.—Total Solute Concentration in the Bar of Alloy B After Nine and Eighteen Passes of the Molten Zone.



the number of passes, as has shown to be justified by the work of Reiss.<sup>2</sup> The number of passes is an integral

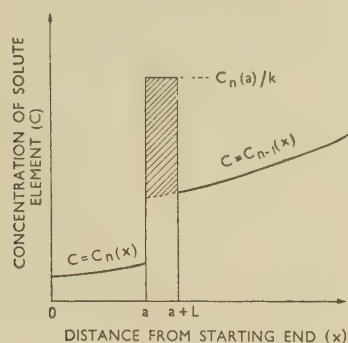


FIG. 5.—Calculation of Flow of Solute Material Across Interface.

quantity, so that for zone-refining equation (2) may be written:

$$\frac{\partial f}{\partial a} = -\{C_n(a) - C_{n-1}(a)\} \quad (3)$$

TABLE VI.—Calculation of the Partition Coefficient for Elements Segregating with the Molten Zone.

Element	Distance from Starting End, mm.	$\frac{dC_n(a)}{da} \times 10^{-3}$	$C_n(a+L)$ , %	$C_{n-1}(a) - C_n(a)$ , %	$C_n(a)$ , %	$\frac{C_{n-1}(a+L) - C_n(a)}{C_n(a)}$ , %	$k$
Chromium . .	25	0.32	0.0018	0.00010	0.0011	0.0008	0.88
Manganese . .	25	0.47	0.0022	0.00035	0.0010	0.00155	0.67
Silicon . . .	25	0.29	0.0019	0.00028	0.0011	0.00108	0.59
Silver . . . .	25	0.26	0.0019	0.00065	0.0012	0.0013	0.44

Differentiating (1) with respect to  $a$  and substituting in equation (3), we get:

$$\frac{L}{k} \frac{\partial C_n(a)}{\partial a} = C_{n-1}(a+L) - C_n(a) \quad (4)$$

Then  $k$  is given by:

$$k = L \frac{\partial C_n(a)}{\partial a} \times \frac{1}{C_{n-1}(a+L) - C_n(a)} \quad (5)$$

## 2. CALCULATION OF THE PARTITION COEFFICIENT

All the terms on the right-hand side of equation (5) can be found from the spectrographic data, and therefore an approximate value for the effective partition coefficient may be calculated. Throughout the following calculations corrected spectrographic values have been employed, using the factors given at the foot of Table IV. However, inspection of equation (5) shows that these factors do not affect the calculated value of  $k$ .

The curves of Fig. 2 were redrawn to a suitable scale, and the gradients for the respective elements were measured at a distance 2.5 cm. from the starting end. By measuring the slope of a tangent drawn at this point, a value for  $\frac{\partial C_n}{\partial a}$  was obtained, as given in Table VI. The value of  $L$  was maintained constant at 2.2 cm.

For elements segregating in the direction of travel of the molten zone, a graph of concentration against number of passes was drawn in order to determine the

value of the denominator in equation (5). From this graph the value of  $C_n(a)$  and  $C_{n-1}(a)$  could be found for  $a = 2.5$  cm. and  $n = 9$ . The change in concentration produced by one additional pass after a number of previous passes was considered to be small enough for it to be assumed that corresponding arcs of length  $L$  of the  $(n-1)$ th and the  $n$ th curve relating concentration to distance along the bar were parallel (Fig. 6). Then:

$$C_{n-1}(a+L) - C_n(a) = C_n(a+L) + \{C_{n-1}(a) - C_n(a)\} - C_n(a) \quad (6)$$

The term in parentheses was determined as described in the previous paragraph and the remaining two terms were obtained from redrawn curves of Fig. 2. These values are recorded in Table VI, together with the calculated value of the partition coefficient obtained by substituting in equation (5).

For the elements iron, cobalt, and nickel, which segregated towards the starting end of the bar, it was not possible to find values of  $C_{n-1}(a+L) - C_n(a)$ , since a satisfactory curve giving the relation of concentration at a given point to the number of passes had not been

obtained. In order to find an approximate value of the partition coefficient, it was assumed that for concentrations greater than the initial value (0.01%) iron and nickel had almost arrived at their ultimate distribution after nine and eighteen passes, respectively. This

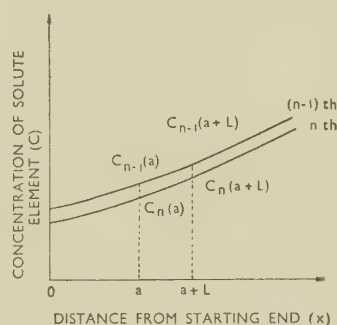


FIG. 6.—Calculation of Partition Coefficient.

assumption was justified to some extent by a comparison of Fig. 2 with Fig. 3 and by comparing both these curves with theoretical curves.<sup>3</sup> This meant that  $C_{n-1}(a) - C_n(a)$  was zero when the concentration of these elements was greater than 0.01% and  $n$  greater than nine and eighteen for iron and nickel, respectively. Values for the partition coefficient have then been calculated (Table VII). No satisfactory treatment could be found for the results obtained with cobalt owing to insufficient analytical data.

## 3. COMPARISON WITH PHASE DIAGRAMS

Phase diagrams for the binary systems of copper with chromium, cobalt, iron, manganese, nickel, silicon, and silver have been published,<sup>5</sup> and from these diagrams an approximate value of the partition coefficient for dilute copper alloys can be obtained.

Tangents were drawn to the solidus and the liquidus curves at their point of intersection, and  $k$  was given by the ratio of the intercepts made by these tangents and the temperature axis with any horizontal line. The

TABLE VII.—Calculation of the Partition Coefficient of Iron and Nickel.

Element	Distance from Starting End, mm.	$\frac{dC_n(a)}{da} \times 10^{-3}$	$C_n(a+L), \%$	$C_n(a), \%$	$\frac{C_n(a+L) - C_n(a)}{\%}$	$k$	$k$ (average)
Iron	25	-9.05	0.0119	0.0245	-0.0126	1.58	} 1.6
	50	-3.56	0.0107	0.0061	-0.0046	1.71	
Nickel	25	-6.20	0.0147	0.0271	-0.0124	1.10	} 1.2
	50	-4.79	0.0052	0.0135	-0.0083	1.27	

TABLE VIII.—Partition Coefficients for Various Elements in Copper.

Element	Partition Coefficient	
	From the Phase Diagrams	From Zone-Refining
Chromium . . . . .	0.50	0.88
Iron . . . . .	2	1.6
Manganese . . . . .	0.70	0.67
Nickel . . . . .	2.6	1.2
Silicon . . . . .	0.38	0.59
Silver . . . . .	0.45	0.44

accuracy of the value of the partition coefficient obtained from the phase diagram was, in some cases, not very great, since the tangents were nearly parallel to the horizontal axis.

In Table VIII the effective partition coefficients calculated from the zone-refining experiments are compared with those obtained from the phase diagrams. There is approximate agreement between the two sets of results, although the values obtained by the zone-refining method tend to be nearer unity. This would suggest that the assumptions upon which the simple mathematical theory of zone-refining is based are not completely fulfilled under the conditions used in these experiments. This is possibly due to some variation in composition of the molten zone, particularly near the freezing interface, and

to equilibrium between the solid and the liquid not being maintained.

Near the freezing interface there is likely to be a solute-rich layer, its width being dependent upon the rate of travel of the freezing interface, the amount of stirring of the liquid zone, and the rate of diffusion of the solute elements in liquid copper.<sup>6,7</sup> The width of a solute-rich layer in the present experiments must, however, have been narrow, owing to the stirring produced by the method of heating and the slow rate of zone travel. It seems likely that the differences between the two values of the partition coefficient given in Table VIII are related to the rates of diffusion of the various elements in liquid copper, efficient segregation corresponding to high rates of diffusion.

## IV.—CONCLUSIONS

The phase diagrams of copper binary systems may be used to estimate the segregation characteristics of alloying elements during zone-refining of dilute copper alloys. No doubt in other materials the behaviour during zone-refining may, to a large extent, be estimated from a knowledge of the appropriate phase diagrams.

The values of the partition coefficients found from the phase diagrams and those calculated from the zone-refining results show approximate agreement. However, the tendency for the amount of segregation to be less than would be expected shows that the theoretical assumptions made are not wholly in accordance with the conditions of the experiments. The assumptions most likely not to be fulfilled are those of homogeneous composition in the liquid phase and equilibrium at the freezing interface.

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# THE NATURE OF SOME MECHANICALLY POLISHED METAL SURFACES AS EVIDENCED BY EPITAXIAL PHENOMENA \*

1739

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## SYNOPSIS

Since the phenomenon of epitaxis might be expected to be sensitive to the presence of thin surface layers, experimental techniques based on it have been used in an endeavour to make a fresh approach to the problem of the existence of a Beilby layer on surfaces polished by mechanical metallographic methods. It is shown that electrodeposits formed on surfaces of copper,  $\alpha$ -brass, tin, zinc, silver, and iron, and the overgrowths of alkali halides on surfaces of silver, are epitaxed after finish polishing by standard methods. However, if misorientations are present in the surface owing to deformation remaining from the abrasion stages of preparation or introduced by an excessively coarse polishing operation, the electrodeposits may not appear to be continuous with the substrate grains when examined in section. This is because the misoriented areas initiate sub-grains in the deposit which, if present in sufficient numbers, destroy the appearance of continuity.

From a consideration of this evidence, it is concluded that the existence of a Beilby layer on the surfaces investigated is unlikely. If present, it would probably have to be either discontinuous or only one or two atom layers in thickness. The probable nature of mechanically polished metal surfaces as suggested by the author's investigations up to this stage is discussed.

## I.—INTRODUCTION

IN an earlier paper,<sup>1</sup> it was shown that there is good reason to believe that fine metallographic polishing operations occur essentially by a cutting process, the metallographic evidence supporting this conclusion now being more convincing than that supporting the alternative and classical theory due to Beilby<sup>2</sup> that polishing occurs by a process of surface flow. Beilby's theory was originally based entirely on metallographic evidence, but it later received considerable support from the observation that metal surfaces polished by mechanical methods gave rise to a characteristic diffuse-halo type of electron-diffraction pattern.<sup>3-5</sup> This was interpreted as evidence of the presence of a liquid-like or "amorphous" layer which Beilby had suggested was smeared across the surface during polishing. Subsequently, there has been some discussion as to whether this layer, usually known as the "Beilby layer", is amorphous or micro-crystalline;<sup>4-6</sup> it has also been suggested that it may contain occluded oxides,<sup>7,8</sup> or be diluted with oxygen atoms,<sup>9</sup> and that these factors might account for the stability of the layer. Irrespective of these considerations of detail, the idea is widely accepted that a layer which is a physically distinct entity and which differs considerably in its characteristics from a macro-crystalline material is present on mechanically polished surfaces. Estimates, based on electron-diffraction evidence, of the minimum thickness of the Beilby layer on metallographically polished surfaces vary from 20 to 50 Å.<sup>5, 10-12</sup>

The author's<sup>1</sup> earlier investigation employed optical microscopy as the method of examination. Consequently, it gave no evidence as to the existence or otherwise of the Beilby layer. Nevertheless, it did suggest

that the classical idea of the layer as a smear across the surface would have to be modified to that of a layer contouring the polishing scratches. Moreover, it indicated that the evidence for the existence of a Beilby layer now rests almost entirely on the interpretation of the halo electron-diffraction patterns. This interpretation is, and always has been, in some dispute (see, for example, Kirchner,<sup>13</sup> Burwell,<sup>14</sup> and Renzema<sup>15</sup>). The purpose of the present work was to make a fresh appraisal of the problem by using a new experimental technique. That chosen was one based on the phenomenon of orientated overgrowth (or epitaxis), a phenomenon which might be expected to be sensitive to the presence of these very thin surface layers. A parallel investigation, by electron-diffraction methods, has been carried out, and the results will be reported elsewhere.<sup>16</sup>

Epitaxy phenomena have been used previously to only a limited extent to investigate this problem. Baker reported,<sup>17</sup> and Beilby confirmed,<sup>2</sup> that crystallites of sodium nitrate formed on polished cleavage faces of calcite are oriented, but subsequent work has shown that these experiments are not relevant to the problem because no evidence of a Beilby layer is found when a polished surface of this type is examined by electron-diffraction methods.<sup>5, 18-20</sup> The epitaxy of electrodeposits on mechanically polished surfaces has been investigated on many occasions. It is invariably reported that the deposits are discontinuous after both industrial<sup>21-25</sup> and metallographic<sup>26-31</sup> methods of preparation, and this fact has been interpreted as evidence that the deposit is not epitaxed and hence as evidence of the presence of a Beilby layer on mechanically polished surfaces.<sup>23, 25</sup> Jacquet,<sup>28, 32</sup> however, has realized that general surface deformation might also be

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responsible for the lack of continuity of the electrodeposits. The present author<sup>33</sup> has found that continuous electrodeposits of copper can be obtained on copper surfaces prepared by at least one method of mechanical metallographic polishing.

## II.—EXPERIMENTAL METHODS

### 1. MATERIALS

The main experiments were carried out on specimens of annealed polycrystalline O.F.H.C. copper (99.98% purity). This material was chosen because it is well established that electrodeposits in which continuity persists for considerable thicknesses can be grown under simple conditions of electrodeposition.<sup>22, 24, 34, 35</sup> Furthermore, it is known that the oxide film which forms during the oxidation of copper surfaces in air is oriented,<sup>36-39</sup> probably being formed merely by the expansion of the pre-existing copper lattice.<sup>36</sup> This eliminates the possibility that failure to obtain epitaxy may be due to the growth of a non-oriented oxide film on the surface.<sup>40</sup>

Subsidiary experiments were carried out on specimens of annealed polycrystalline brass (containing 30.1% zinc), zinc (99.9% purity), tin (99.9% purity), silver (99.99% purity), and an ingot iron (99.9% purity); this represents almost the complete range of metals on which continuous electrodeposits can be grown under simple conditions. The oxide layers formed on zinc<sup>41, 42</sup> and iron<sup>36, 43</sup> in air are known to be oriented, but little information is available on those formed on brass and tin, although it has been reported that in the latter case the oxide is amorphous.<sup>44</sup> Johnson's<sup>40</sup> results indicate that any discrete film of oxide formed on silver in air is probably oriented. The deposits formed on the brass and zinc surfaces were of considerable interest because the deformed layer produced on these metals during polishing has been investigated in detail.<sup>1</sup>

### 2. PREPARATION OF THE TEST SURFACES

Mounted specimens were abraded and rough-polished by methods which are known to produce a surface free from gross deformation,<sup>1, 45</sup> and were finish-polished by a number of representative metallographic methods; the definition of a metallographic polishing process adopted for the purpose of the present work has been given elsewhere.<sup>1</sup> The polishing pads used were:

(a) A (0-1)  $\mu$ -grade diamond abrasive charged as an impregnated paste on a synthetic suede cloth lubricated with kerosene.

(b) A (0-2)  $\mu$ -grade  $\alpha$ -alumina abrasive used as a water suspension on a "Selvyt" cloth pad.

(c) A (0-0.3)  $\mu$ -grade  $\alpha$ -alumina abrasive used as for (b).

(d) A (0-0.1)  $\mu$ -grade  $\gamma$ -alumina abrasive used as for (b).

(e) A calcined grade of magnesium oxide used as for (b); this is termed the "normal" method of polishing on magnesium oxide.

The specimens were polished by hand for about 5 min., and were finished so that a unidirectional system of scratches was obtained. The specimens were washed in running warm water and then in acetone, and were dried with a blast of cold air.

All these surfaces were specularly reflecting at normal incidence and appeared generally to be scratch-free when examined microscopically under bright-field illumination, although occasional isolated scratches could be detected with the coarser finishes. Numerous scratches were detectable in all cases under phase-contrast illumination, the range being illustrated in Figs. 1 and 2 (Plate XXXIII).

In a subsidiary series of experiments, surfaces were prepared by polishing specimens on a (0-1)  $\mu$ -grade diamond abrasive pad (as in (a) above) followed by "skidding" on a magnesium oxide paste.<sup>45</sup> Previous work<sup>1</sup> has suggested that the latter polishing method probably operates by a mechanism of etch attack. It is safest for the present purposes, therefore, to regard it as an etching method by which thin layers can be removed uniformly from the surface with a reasonable degree of control. The rate of removal in the case of 70:30 brass is estimated to be about 0.05  $\mu$ /min. for a water paste of magnesium oxide, and about 0.15  $\mu$ /min. for a paste containing 5 g./l. ammonium persulphate in solution; the polishing rate for copper is not known, but is assumed for the present purposes to be the same as that for brass. This series was prepared with a view to investigating the characteristics of various levels beneath the surface polished on the (0-1)  $\mu$ -grade diamond pad; it is not suggested that these surfaces are of the type which classical theory suggests should contain a Beilby layer.

### 3. CONDITIONS OF ELECTRODEPOSITION

Most of the experiments were carried out on electrodeposits formed on the polished surfaces. Electrodeposition of copper on the copper and brass specimens

TABLE I.—Conditions of Electrodeposition.

Metal Deposited	Solution	Temp., °C.	Current Density, amp./dm. <sup>2</sup>	Reference
Copper	CuSO <sub>4</sub> .10H <sub>2</sub> O, 200 g./l.; H <sub>2</sub> SO <sub>4</sub> (1.81 sp. gr.), 37 g./l.	20	3.0	...
Zinc	ZnSO <sub>4</sub> .7H <sub>2</sub> O, 350 g./l.; NH <sub>4</sub> SO <sub>4</sub> , 30 g./l.; pH < 4	20	2	...
Tin	SnSO <sub>4</sub> .2H <sub>2</sub> O, 100 g./l.; H <sub>2</sub> SO <sub>4</sub> (1.81 sp. gr.), 30 g./l.; Tartaric acid, 30 g./l.; Gelatin, 4 g./l.; Cresol 6 g./l.	20	1.5	...
Silver	AgCN, 35 g./l.; KCN, 30 g./l.; K <sub>2</sub> CO <sub>3</sub> , 38 g./l.	20	0.5	Setty and Wilman <sup>61</sup>
Iron	FeCl <sub>2</sub> .4H <sub>2</sub> O, 600 g./l.; pH $\approx$ 1.8	70	0.5	James <sup>62</sup>

was carried out in a standard acid copper sulphate bath (see Table I), two investigational techniques being employed:

(a) A thin deposit was formed on the test surface by deposition at a current density of 0.3 amp./dm.<sup>2</sup> for about 30 sec. and the deposit examined by optical microscopy. Two features are to be expected of an



epitaxed deposit. First, the deposit should be composed of small crystallites of regular shape and orientation on each substrate grain.<sup>28</sup> Secondly, the density of the crystallites deposited should vary with the orientation of the substrate grain;<sup>35</sup> consequently, the grain structure of the substrate surface should be delineated by the deposit.

(b) A heavy deposit was formed at a current density of 3.0 amp./dm.<sup>2</sup> and the specimen sectioned normal to the scratch system on the test surface. This section was mechanically polished,<sup>45</sup> etched in a ferric chloride reagent, and examined metallographically. Epitaxy in this instance should be evidenced by "continuity" between the grains of the deposit and substrate.

The remaining metals were investigated only by the technique of the examination of sections of heavy deposits, the conditions of electrodeposition used being set out in Table I. Some of these plating baths were developed specifically to give epitaxed deposits, and in these instances the recommended conditions were adhered to rigidly. In all cases, it was confirmed that completely continuous deposits were obtained on a heavily etched surface of the metal concerned. As a precaution against etching of the surface by the plating solutions, the specimens were always immersed in the plating bath with the full plating potential applied. The surfaces were degreased by immersion in a cold organic solvent before plating, but were not treated in any other way.

### III.—THIN ELECTRODEPOSITS FORMED ON POLISHED SURFACES OF COPPER AND BRASS

The deposit formed on a comparatively coarsely-polished surface of either copper or brass, such as those obtained by polishing on (0-1)  $\mu$ -grade diamond, showed only traces of evidence of a relationship with the substrate grains when examined under bright-field illumination (Fig. 3, Plate XXXIII). However, stronger evidence of a relationship could be established by examination under polarized light (Fig. 4, Plate XXXIII). From the accepted interpretation of this type of response to polarized light,<sup>46-48</sup> it may be concluded that the crystallites on individual grains show at least some degree of regularity in form and orientation. With progressively finer polishes, the evidence of a relationship between the deposit and the substrate grains became progressively stronger. The substrate grains were obviously delineated by the deposit (Fig. 5, Plate XXXIII), and the grain contrast observed under polarized light increased correspondingly (Fig. 6, Plate XXXIII).

Attempts were made to resolve the crystallites of these deposits and so confirm the above deductions as to their regularity in shape and orientation, but all were unsuccessful. The crystallites were too small and their thickness was too great for satisfactory resolution by optical microscopy, and the plated surfaces were too rough for replicas to be stripped successfully for electron microscopy. Certain features were observable, however, by optical microscopy at high magnifications. The deposit crystallites were comparatively widely spaced, and were present on all grains with even the shortest deposition times (Fig. 7, Plate XXXIII). They formed

preferentially along the polishing scratches (a feature which has been observed previously<sup>23,28</sup>), appearing to form at the edges of the scratches rather than within the scratches themselves (Fig. 7). The surface appeared to be covered mostly by the lateral growth of the original crystallites, although some additional crystallites did form.

Deposits formed on surfaces which had been finished by skidding on a paste of magnesium oxide differed in several respects from those already discussed. The crystallites of the deposit were much more closely spaced and, at first, little or no deposit formed on some grains (Fig. 8, Plate XXXIII). Nevertheless, preferential deposition still occurred at what appeared to be the sites of the pre-existing diamond abrasive scratches (Fig. 9, Plate XXXIV). The latter micrograph is of a brass surface from which about 0.5  $\mu$  had been removed from a (0-1)  $\mu$ -grade diamond finish by a skidding treatment; the appearance of a copper surface after the same treatment was very similar. No evidence of preferential deposition at the scratch sites was found in either case after the removal of 0.8-0.9  $\mu$  from a surface of this type. Attention is drawn to the similarity in appearance between Fig. 9 (Plate XXXIV) and the micrographs of surfaces of brass prepared in the same manner but etched in a ferric chloride reagent (see Fig. 16, Plate XI, of the earlier paper<sup>1</sup>). This suggests that the preferential deposition occurs at bands of locally deformed material in the surface remaining from the rays of deformation associated with the polishing scratches; furthermore, it seems that preferential deposition occurs only when the remnants are present of what has been termed the "surface zone of severest deformation".<sup>1</sup>

A few experiments were also carried out with surfaces which had been polished on (0-1)  $\mu$ -grade diamond abrasive and then finished by heavy chemical etching or by electrolytic polishing. The results were identical with those obtained on surfaces finished by skidding on the magnesium oxide pads. In the case of electrolytic polishing, of course, the preferential deposition at scratch traces was shown only after very short polishing times (<1 min.).

### IV.—EXAMINATION OF SECTIONS OF HEAVY DEPOSITS FORMED ON POLISHED SURFACES OF COPPER AND BRASS

#### 1. DEPOSITS ON AS-POLISHED SURFACES

The deposit formed on a surface of copper polished on a (0-1)  $\mu$ -grade diamond abrasive showed no evidence of continuity with the substrate grain, consisting of many fine grains (Fig. 10, Plate XXXIV). The deposits formed on all of the more finely finished surfaces, however, did show evidence of at least restricted continuity. Each substrate grain gave rise to a recognizable continuous primary grain in the deposit, but this primary grain was broken up by features which will be termed "sub-grains" (Fig. 11, Plate XXXIV), their nature being considered in more detail in Section V. Partial continuity of this type does not appear to have been reported previously. The number of sub-grains in each primary grain decreased markedly with increasing fineness in the polish of the substrate surface (Figs. 11-13, Plate XXXIV), only a few small sub-grains being present on surfaces finished on a normal magnesium oxide pad (Fig. 13, Plate XXXIV).

It will be apparent, from a comparison between Fig. 12 (Plate XXXIV) and Fig. 2 (Plate XXXIII), that full continuity in the deposit was obtained at many areas which contained fine polishing scratches.

It seems possible, from backwards extrapolation of the series of micrographs Figs. 11–13 (Plate XXXIV), that the deposit formed on surfaces polished on a (0–1)  $\mu$ -grade diamond abrasive did not appear to be continuous because of the presence of excessive numbers of sub-grains. This suggestion is supported by the observations made on thin deposits (Section III) which did give some evidence of epitaxy on this surface. In this event, it would be necessary to make a distinction between the epitaxy and the continuity of electrodeposits as observed in section; the individual sub-grains could be epitaxed whilst the deposit as a whole is non-continuous.

Removal of the surface layers of a specimen polished on a (0–1)  $\mu$ -grade diamond pad by skidding on a magnesium oxide pad did not necessarily ensure the formation of a completely continuous deposit, sub-grains being present when less than a certain thickness had been removed. For example, sub-grains were fairly numerous when about 0.5  $\mu$  had been removed from the surface (Fig. 15, Plate XXXIV), and complete continuity was not obtained until about 1.0  $\mu$  had been removed (Fig. 16, Plate XXXIV); this is many orders of magnitude greater than the estimated thickness of the supposed Beilby layer.<sup>5, 10–12</sup> Exactly similar qualitative results were obtained when the surface layers were removed by either chemical etching or electrolytic polishing.

The same general results were obtained with brass surfaces, although continuity was not recognizable in this case until the (0–0.1)  $\mu$ -grade alumina finish (Fig. 17, Plate XXXV); almost complete continuity was obtained with a normal finish on magnesium oxide (Fig. 18, Plate XXXV). Fig. 17 (Plate XXXV) is of interest in that so many sub-grains are present that the continuity of the deposit grains is only just recognizable. This field would appear to represent a stage close to that proposed above at which the appearance of continuity is lost. Note also that thin deposits formed on this surface showed strong evidence of epitaxy very similar to that illustrated in Figs. 5 and 6 (Plate XXXIII). When successively thicker layers were removed from a brass surface polished on a (0–1)  $\mu$ -grade diamond abrasive by skidding on magnesium oxide, a few sub-grains only were present after the removal of about 0.3  $\mu$  from the surface (Fig. 19, Plate XXXV), and none was present after the removal of about 0.6  $\mu$ . When these results are compared with those of the earlier investigation,<sup>1</sup> the conclusion is again reached that the sub-grains are initiated by the surface zone of severest deformation produced during polishing, or by remnants of it.

Direct confirmation of this conclusion was obtained from the examination of taper sections of the deposit formed on a surface prepared as for Fig. 19 (Plate XXXV). The sub-grains in the deposit could be seen to have been initiated by residual tips of rays of the surface zone of severest deformation (see Fig. 20, Plate XXXV, which is explained by the sketches in Fig. 33).

At this stage, it is possible to advance the following hypothesis to explain the experimental observations. The individual crystallites first deposited on these polished surfaces are all epitaxed. The orientation in the neighbourhood of a polishing scratch in the surface is

different from that of unscratched (or less severely scratched) areas,<sup>1</sup> and this difference will be reproduced in the deposit crystallites. If the orientation differences are slight, the various crystallites combine as they grow into a single, if somewhat strained, continuous grain in the deposit. If, however, the orientation difference exceeds a certain amount, the crystallites formed along a particular scratch may unite to form a recognizable sub-grain in the primary grain of the deposit.

Since it is to be expected that the misorientation associated with a polishing scratch would be greater the heavier the scratch, it follows that a scratch must exceed a certain more or less critical size before it can

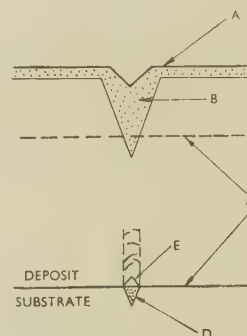


FIG. 33.—Sketch Explaining the Micrograph shown in Fig. 20 (Plate XXXV). (a) Taper section of surface polished on (0–1)  $\mu$ -grade diamond abrasive; (b) taper section after skidding on magnesium oxide and electroplating; this is the state of the section shown in Fig. 20.

#### KEY

- A Surface scratch produced by diamond abrasive.
- B Ray of deformation associated with the polishing scratch.
- C Surface level after skidding on magnesium oxide.
- D Residual tip of the ray of deformation.
- E Sub-grain in the electrodeposit.

initiate a sub-grain under a particular set of experimental conditions. In the case of copper and brass finished on a normal magnesium oxide pad, few scratches exceeding the critical size can be present, but coarser finishes contain progressively larger numbers of scratches exceeding the critical size, and the deposits formed on them contain progressively larger numbers of sub-grains. It is suggested that, eventually, so many sub-grains form that all evidence of continuity between deposit and substrate grain is lost, even though each sub-grain itself may be epitaxed with respect to the point on the surface at which it was nucleated.

The nature of the deposits found when progressively greater thicknesses were removed from an as-polished surface is also consistent with this hypothesis. The strain level, and hence the degree of the local misorientation in the ray of deformation associated with a surface scratch, decreases with increasing depth beneath the surface. It is to be expected, therefore, that the number of sub-grains would decrease as greater amounts are removed from the surface, and this was observed. Moreover, complete continuity is obtained after the removal of only the surface zone of severest deformation, residual strain of a low order still being present;<sup>1</sup> this supports the suggestion that a local misorientation must exceed a certain amount before a sub-grain is initiated.

It follows that it cannot necessarily be assumed that a Beilby layer is present on a polished surface because no evidence of continuity is found in a section of an electro-



deposit formed on that surface. On the other hand, the fact that obviously epitaxed deposits can be obtained on some mechanically polished surfaces may be evidence that a Beilby layer is not present on these surfaces. The validity of the latter conclusion will be considered in a number of the succeeding sections of this paper. First, however, another possible origin of the sub-grains in non-continuous deposits will be considered.

## 2. THE EFFECT OF GROSS SURFACE DEFORMATION

The feature which probably distinguishes most sharply the surfaces investigated here is that they are known to be free from gross deformation remaining from the abrasion stages of preparation.<sup>1</sup> Surfaces investigated by most earlier workers probably contained remnants of this deformation which might well be expected to be a prolific source of sub-grains.

In order to check this possibility, specimens of copper were abraded on silicon carbide papers to the 600 grade and were then polished on (0-0-1)  $\mu$ -grade alumina until the abrasion scratches were just removed completely. A surface of this type would certainly contain severe deformation due to the abrasion treatment,<sup>1</sup> yet is one on which an epitaxed deposit can be expected. The deposits formed on these surfaces showed no evidence of continuity with the substrate (Fig. 14, Plate XXXIV, which can be compared with Fig. 12, Plate XXXIV). This evidence also supports the contention that non-continuity in a sectioned deposit is not necessarily evidence of absence of epitaxy.

## 3. THE EFFECT OF TIME DELAY BETWEEN POLISHING AND ELECTRODEPOSITION

It has been reported<sup>49-51</sup> that the diffuse-halo electron-diffraction pattern obtained on freshly-polished surfaces and taken as evidence of the presence of a Beilby layer sharpens gradually on ageing of the specimen; this has been interpreted as indicating recrystallization of the Beilby layer. Nonaka and Kohra<sup>51</sup> have reported that a fully-sharpened pattern is obtained after ageing polished copper specimens at room temperature for about 100 hr. In the experiments described in Section III, in which electrodeposited overgrowths were examined, the deposits were formed within 1 min. of polishing, so that the question of recrystallization of the Beilby layer scarcely arises. In the case of the heavy deposits discussed in the present section, however, deposition often had to be delayed until several hours after polishing, and it might be argued that partial recrystallization of a Beilby layer could have occurred in this time. The recrystallization could also have been accelerated by the slight heating of the surface during washing after polishing.

A number of the more critical experiments on the copper specimens were therefore repeated individually, so that precautions could be taken to ensure that deposition was started with the minimum delay (about 30 sec.) and that the surface was not heated in any way in the interim. The degree of continuity found in these specimens was in no way different from that found in the specimens discussed previously.

Furthermore, the degree of continuity did not alter significantly in specimens stored in dry air for up to 400 hr. before plating. If the sub-grains found in the

deposits had been due to the presence of local patches of Beilby layer, some reduction in the number of sub-grains might have been expected. It is also apparent that the oxide film formed on the surface during this period, which probably would be over 50 Å. thick,<sup>52</sup> has not interfered with the continuity of growth of the deposit.

## V.—THE NATURE OF THE "SUB-GRAINS" IN THE ELECTRODEPOSITS

It is implicit in the theory advanced in Section IV.1 that the features found in the primary grains of the deposits are crystalline areas which merely differ in orientation from the main grain, and for which the use of the term "sub-grain" seems to be appropriate. In view of the ease with which twins could be initiated in the electrodeposits by stacking faults<sup>53</sup> if they were present in the neighbourhood of a polishing scratch, it is also possible that the features may be twins, although this does not affect seriously the arguments advanced. What must be considered is the possibility that the features may each be a group of minute crystallites such as could be imagined to be initiated by localized patches of Beilby layer. It can be stated from the outset, however, that it is difficult to see, if this were so, why apparently similar features were found in deposits formed on surfaces which had been etched after polishing.

Examination of the features in the copper electrodeposits at high magnification supported the original interpretation (Fig. 21, Plate XXXV). They appeared to be areas which differed only slightly in etching rate from the matrix of the primary grain of the deposit, and gave no evidence of differential colour etching as is shown by a definite twin in the deposit (a twin is present in the field of Fig. 21). The resolution of the features was adequate to discount the possibility that they were composed of groups of very fine grains.

More definite evidence was obtained on this point from the examination of the zinc deposits, which are discussed in more detail in Section VII. Each "sub-grain" unit showed strong and uniform contrast under polarized light and each showed reversed contrast with respect to the matrix grain of the deposit when the specimen was rotated through 90° in an exactly similar manner to the macro-twins in the substrate grains (cf. Figs. 28 and 30, Plate XXXVI). It follows that the units are crystalline and in a twin orientation with respect to the matrix grain. This is precisely what is to be expected from the theory advanced above, because the surface deformed zone associated with polishing scratches in this material is known to be twinned.<sup>1</sup>

Further confirmatory evidence indicating that sub-grains can be initiated in an electrodeposit by locally deformed areas in the substrate surface was obtained by examining deposits formed on specimens of copper and brass which had been subjected to prior deformation. Cylinders of the material were compressed by hammering and then sectioned parallel to the compression direction; this section was polished by electrolytic methods before electrodeposition.

In agreement with the observations of previous workers,<sup>21, 24</sup> the deposits on the copper specimens showed complete continuity after even the severest prior deformation. The continuity was quite clear after 60% compression (Fig. 22, Plate XXXV), and was even

detectable after 80% compression. This is consistent with the theory proposed above because earlier work<sup>54</sup> has shown that the individual grains of copper deform in a comparatively homogeneous manner under these conditions.

Brass, on the other hand, deforms in compression in an inhomogeneous manner in which slip tends to be concentrated in bands of lamellar slip, the traces of which can be developed readily as "slip-band indications" by metallographic etching.<sup>54</sup> Since the orientation in these bands must differ from that of the matrix crystals in somewhat the same manner as the deformed zone associated with a polishing scratch, it is to be expected from the theory advanced earlier that they would initiate sub-grains in an electrodeposit. This was found to be so. A typical example for a 70 : 30 brass specimen is shown in Fig. 23 (Plate XXXV). Note, moreover, that only the major slip-band indications etched in the substrate are associated in the deposit with a feature similar to those which have been referred to as sub-grains, confirming that a significant misorientation is necessary for the development of a discrete sub-grain.

The presumed sub-grains initiated by slip bands in 70 : 30 brass are narrow, and could not be resolved any more clearly than the sub-grains which grew on polished surfaces. In the case of 90 : 10 brass, however, the slip bands, and hence the sub-grains in a covering electrodeposit, are much wider.<sup>54</sup> It was then possible to resolve the sub-grains fairly clearly (Fig. 24, Plate XXXV), and to show that they were an entity reproducing all the structure of the slip-band indications.

A further feature observed with the specimens of deformed brass was that, in a thin overgrowth deposit formed on an electrolytically polished surface, preferential deposition occurred at the traces of the lamellar slip bands. It is general experience that deposition occurs preferentially at areas of high strain, and this would account for the preferential deposition which occurred at the sites of both these slip bands and the polishing scratches in mechanically polished surfaces.

#### VI.—EPITAXY OF ALKALI HALIDE OVERGROWTHS ON MECHANICALLY POLISHED SURFACES OF SILVER

The conclusion that the formation of epitaxed electrodeposits on some mechanically polished surfaces may indicate the absence of a Beilby layer on these surfaces may be criticized on two further grounds. First, it could be argued that, in spite of the precautions taken, the Beilby layer may have been etched away by the plating bath before deposition began. Secondly, it has been suggested by Wilman<sup>55</sup> that the surface may be heated to substantial temperatures during electrodeposition, and it might just be possible that this heating effect caused recrystallization of a Beilby layer at a sufficiently early stage to enable the formation of epitaxed deposits.

Both these objections would be met if overgrowths of alkali halides formed from solution on as-mechanically polished surfaces were oriented, since it can scarcely be imagined that either of the above effects could occur under these experimental conditions. Johnson<sup>40, 56-58</sup> has investigated this phenomenon extensively, using etched metal surfaces, and has shown that the most

suitable combination with which to demonstrate the effect is that of sodium chloride deposited on a silver surface by the rapid evaporation of a saturated alcoholic solution.

It was found that the overgrowths of sodium chloride formed in this manner on surfaces of silver finely polished as described in Section II.2 were, in fact, oriented; Figs. 25 and 26 (Plate XXXVI) show typical results obtained after polishing on (0-0.1)  $\mu$ -grade alumina. The individual grains of the substrate were distinguished by differing densities of deposited crystallites (Fig. 25), and the crystallites formed on individual twin areas were of regular orientation (Fig. 26), the regularity being as strict as that shown in Johnson's illustrations. Some preferential deposition occurred at the sites of the more marked polishing scratches, but these crystallites appeared to be just as strictly aligned as those deposited elsewhere. It would be difficult to detect small misorientations of these crystallites.

#### VII.—EXAMINATION OF SECTIONS OF HEAVY DEPOSITS FORMED ON POLISHED SURFACES OF OTHER METALS

The only difference found between the deposits formed on polished surfaces of the remaining metals investigated and those formed on the copper surfaces was in the fineness of polish required to give recognizable continuity in the deposit. Continuity was recognizable much earlier in the case of the metals of lower melting point, tin and zinc. For tin, complete continuity was found even after polishing on (0-1)  $\mu$ -grade diamond (Fig. 27, Plate XXXVI); the continuity on zinc surfaces was recognizable after the same treatment (Fig. 28, Plate XXXVI), and was almost complete after polishing on (0-0.1)  $\mu$ -grade alumina, although a few very fine twin sub-grains were still present (Fig. 29, Plate XXXVI). On the other hand, the coarsest polish which resulted in recognizable continuity on surfaces of silver and iron was that obtained on (0-0.1)  $\mu$ -grade alumina (Figs. 31 and 32, Plate XXXVI); in both cases, however, the continuity was then slightly more obvious than that obtained on 70 : 30 brass surfaces polished by the same method (Fig. 17, Plate XXXV). It is again apparent that it is more difficult to recognize epitaxy in sections of heavy electrodeposits than by the examination of thin overgrowths (cf. Figs. 25 and 31, Plate XXXVI).

The higher degree of continuity obtained on the tin and zinc surfaces must indicate either that the local misorientations introduced during polishing are less marked or that they are relieved (without recrystallization) soon after polishing. The latter is the more likely, although both factors may contribute. If strain relief is the most significant factor, it follows that all the misorientations in a polished tin surface are relieved to a level below that which would result in the initiation of sub-grains in the deposit. In the case of zinc, the misorientations associated with the minor scratches may be relieved similarly, but the twins produced at the sites of the major scratches are not affected and are responsible for all the sub-grains found. Twinning does not seem to be produced in tin surfaces during polishing. It is not possible, at this stage, to explain the difference in the degree of continuity found in similarly polished surfaces of the metals of high melting point, but it is



presumably associated with small differences in the degree of misorientation produced by a particular size of abrasive particle whilst cutting.

### VIII.—DISCUSSION

The first significant conclusion which can be drawn from the present investigation is that the fact that electrodeposits formed on some mechanically polished surfaces do not appear to be continuous with the substrate when examined in section is not necessarily evidence that the deposit is not epitaxed, and therefore is not evidence that a Beilby layer is present on the surface. It has been established that non-continuity in an epitaxed deposit can result from the presence of local misorientations in the surface; the misorientations may be due to deformation remaining from the abrasion stages of preparation or to deformation introduced during the polishing operation itself. The misorientations are reproduced in the deposit and may initiate discrete sub-grains in the primary continuous grains of the deposit. When present in sufficient numbers, the sub-grains destroy the appearance of continuity. Both these sources of misorientations can be reduced in mechanically polished surfaces to a level sufficiently low to give almost completely continuous deposits if suitable precautions are taken during preparation.

The deposits obtained on the finer polished surfaces were certainly epitaxed over extensive areas containing numerous polishing scratches, and there is good reason to believe that the deposits on the surfaces investigated were all epitaxed locally. A possible interpretation of this evidence is that a Beilby layer is not present on the surfaces concerned. Several objections to this interpretation based on details of experimental technique have been discussed in the text, but other interpretations are still possible if the current concept of the Beilby layer is modified substantially.

First, the above interpretation assumes that the crystal orientating forces could not extend through, or at least would be seriously affected by, a disorganized layer such as the Beilby layer is imagined to be. Beilby,<sup>2</sup> to explain Baker's<sup>17</sup> observations, proposed that the orienting forces could, in fact, extend through the layer. It is now recognized, however, that the range of these forces is very short and probably not more than the order of an atomic diameter;<sup>59</sup> one or two atom layers would therefore appear to be the upper limit for the thickness of a Beilby layer which would not affect the growth of epitaxed deposits. Although it could be supposed that the Beilby layer is of this order of thickness, this would not be consistent with electron-diffraction evidence, which suggests that the layer, if it exists, is at least 20 Å. thick in the case of metallographically polished surfaces.<sup>5, 10-12</sup>

Secondly, the present experimental evidence can be explained if it is supposed that the Beilby layer is discontinuous. It could then be argued that the crystallites from which the deposits grow are nucleated only at the areas free from Beilby layer,\* although it is rather difficult to see why this should be so because the usual experience is that preferential deposition occurs at the most highly strained areas in a surface. This sugges-

tion, however, would be more consistent with the electron-diffraction evidence than the one discussed above. The patches of Beilby layer can be assumed to be of appreciable thickness, and probably only a comparatively small number of patches would have to be present to give rise to an overriding diffuse diffraction pattern at the low angles of incidence used in this method of examination.

Once it is admitted that polishing occurs essentially by a cutting mechanism—and it is almost certain that this is so—it is difficult to imagine why the Beilby layer should be discontinuous. The first and most reasonable assumption which might be made is that a continuous Beilby layer is produced in the groove of a polishing scratch during cutting. If a polished surface contained only comparatively few scratches, it might then be supposed that the areas between the scratches are the areas free from Beilby layer. However, it is impossible to imagine a surface prepared by a cutting process which removes a layer of appreciable thickness—as all the processes under consideration do—as being anything other than a system of intimately overlapping scratches; i.e. the surface is composed entirely of scratch grooves. It must be assumed, therefore, either that the Beilby layer originally produced in a scratch groove is discontinuous, or that it breaks up within a very short time. It is also to be noted that these more complicated explanations are necessary only to maintain the interpretation that the halo electron-diffraction pattern usually obtained from mechanically polished surfaces is evidence of the presence of a Beilby layer. It has been indicated already that this interpretation is by no means unambiguous, but the discussion of this point will be left for a later publication.<sup>16</sup>

The results also have a bearing on the hypothesis advanced by Bowden and Hughes<sup>60</sup> that the polishing of metals occurs by local surface melting, the molten material solidifying to form the Beilby layer. Earlier work by the present author<sup>1</sup> has indicated that surface melting can scarcely play a major part in the polishing of metals, although there is at present no reason to suggest that it might not occur on a minor scale. If it does, the present results suggest that there is good reason to believe, within the limitations already discussed, that the molten material solidifies in an epitaxed manner, continuing all the local misorientations introduced by the primary polishing process of surface cutting. In this event, the solidified material would be indistinguishable from material that had never melted.

The author's work to this stage, then, indicates that the structure of a surface polished by mechanical metallographic methods is as follows, the various layers which can be distinguished in the surface being discussed in succession:

(1) *Beilby Layer* (maximum depth of the order of tens of Ångström units).—The presence of a Beilby layer on the surfaces under consideration appears to be unlikely. If it does exist, the layer would probably have to be regarded either as being only one or two atom layers thick or as being discontinuous. Moreover, it would have to be thought of as a layer contouring the polishing scratches instead of as a smooth smear across the surface.

(2) *Layer of Severest Deformation* (depth of the order

\* The recent work of Déo *et al.*<sup>63</sup> confirms that a fully epitaxed deposit would still be obtained if this occurred,

of tenths of microns).—Probably a shear zone at the surface which may have been deformed at elevated temperature. The present experiments do not provide any information on the maximum strain in this layer because the epitaxial phenomenon is sensitive only to local differences in strain.

(3) *Layer of Minor Deformation* (depth of the order of microns).—A layer which contains strains of a low order of magnitude introduced during polishing. This deformation is localized, extending in rays beneath the polishing scratches; the layer of severest deformation also shows a tendency to be localized in similar rays.

(4) *Layer of Gross Deformation* (depth of the order of tens of microns).—A layer which contains strains which may be of a high order of magnitude and which are the remnants of the deformed layer produced during preliminary abrasion; the layer overlaps the layer of minor deformation. The depth of this layer, and the maximum strain in it, may vary considerably, depending upon the exact method of preparation. It may be eliminated completely by adopting suitable preparation procedures.

In addition, most surfaces prepared by mechanical methods are likely to be covered either partially or completely with a thin layer of oxide or, possibly, other corrosion products. The fresh nature of the surface exposed by a cutting process and the possibility of high surface temperatures during cutting make this inevitable. The present work has indicated, however, that the oxide

(or corrosion product) would be oriented on the surface whenever this is possible.

The above remarks apply to any mechanical method of polishing which occurs essentially by a cutting mechanism. Some special polishing methods appear to occur either partly or wholly by a mechanism of etch attack; examples are those processes which incorporate an etching reagent in the abrasive suspension and probably also the skidding method on magnesium oxide. These polishing methods do not appear to introduce layers of the second and third types. They therefore offer an opportunity of removing layers of this type produced by earlier polishing operations of the cutting type. The presence of a Beilby layer after polishing by these methods is also even less likely than after a cutting process. Consequently, although these processes cannot be regarded for theoretical purposes as being true mechanical methods of polishing, they probably do represent methods by which physically true surfaces can be prepared whilst retaining the advantages of mechanical methods of polishing.

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# THE INFLUENCE OF HEAT-TREATMENT ON THE ELECTRICAL RESISTIVITY AND THE THERMAL CONDUCTIVITY OF ELECTRODEPOSITED CHROMIUM \*

1740

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(Communication from the National Physical Laboratory)

## SYNOPSIS

The thermal and electrical conductivities of electrodeposited chromium are shown to increase as a result of heat-treatment. A detailed investigation of these properties has been made over a wide range of temperatures and for heat-treatment temperatures extending to 1410° C. After heat-treatment at 1410° C. the thermal conductivity at 50° C. was 3.65 times the original value for the as-deposited material. From consideration of the relationship between the thermal and electrical conductivities, the conclusion is reached that the thermal conductivity appears to have a considerable lattice component which is a function of heat-treatment as well as of temperature.

The well-known normal-temperature anomaly in the properties of chromium became apparent in the resistivity/temperature curve only after heat-treatment at 545° C. This anomaly is discussed in some detail, and the tentative suggestion is made that it may be associated with the presence of chromic oxide.

## I.—INTRODUCTION

THE work of Brenner, Burkhead, and Jennings<sup>1</sup> has shown electrical resistivity to be one of the many physical properties of electrodeposited chromium that is strongly influenced both by the conditions of deposition and by subsequent heat-treatment. The electrical resistivity of chromium is of further interest in view of an anomaly in the variation of this property with temperature. This anomaly has been observed by several workers,<sup>2-8</sup> and has also been reported for other properties of chromium, such as thermal expansion,<sup>9</sup> thermoelectric power,<sup>6</sup> and the elastic constants.<sup>7, 10</sup> A satisfactory explanation, however, is still awaited.

In comparison with the electrical conductivity, relatively little attention has been directed towards the thermal conductivity of chromium. Tables of physical constants<sup>11, 12</sup> quote a value of 0.165 cal. cm./cm.<sup>2</sup> sec. °C. (0.69 joule cm./cm.<sup>2</sup> sec. °C.), but its origin is not given and does not appear to be readily available. Experimentally determined values of Söchtig<sup>5</sup> and of Powell and Hickman<sup>13</sup> differ appreciably from this value. The latter workers obtained results ranging from 0.36 to 0.32 joule cm./cm.<sup>2</sup> sec. °C. over the temperature range 35°–73° C., for an electrodeposited coating formed as a disc on the end of a metal bar. Heat-treatment would be expected, in the light of the work of Brenner *et al.*,<sup>1</sup> to lead to higher values, but cracking of the disc on heating prevented further work being undertaken on this sample. Söchtig's results for a sample of electrolytic chromium which measured only  $0.7 \times 0.23 \times 0.21$  cm. and which had been heat-treated for 30 min. at 1000° C. are reproduced in Table I.

In view of the fact that the sample had been heat-

treated, these lower conductivity values are surprising. Another unusual feature is the sharp fall in the Lorenz function with increase in temperature when the values

TABLE I.—Söchtig's Data for Electrolytic Chromium, Heat-Treated for 30 min. at 1000° C.

Mean Temperature, °C.	Thermal Conductivity, joule cm./cm. <sup>2</sup> sec. °C.	Electrical Resistivity, microhm cm. <sup>2</sup> /cm.	$10^8 \times$ Lorenz Function, joule ohm./sec. °C. °K.
–77.5 <sub>5</sub>	0.344	13.4	2.36
0.5 <sub>5</sub>	0.292	21.2	2.26
26.0	0.266	22.5	2.00
43.5	0.262	22.5	1.86
60.9 <sub>5</sub>	(0.279)	23.6	(1.97)

are still below  $2.45 \times 10^{-8}$ , Sommerfeld's theoretical value.

The main purpose of the present work was to provide experimental results for the thermal conductivity and electrical resistivity of a tube of electrodeposited chromium and to study the changes brought about in both properties after the sample has been heated to various temperatures extending up to 1410° C. Some electrical-resistivity measurements were, however, carried out on flakes of chromium and these will be first described.

## II.—EXPERIMENTS ON FLAKES OF ELECTRODEPOSITED CHROMIUM

The flakes of chromium, obtained from Messrs. Johnson, Matthey and Co., Ltd., were from 0.013 to 0.02 cm. in thickness. Some were freshly deposited and were stated to contain 0.8–1.0% oxygen; others had

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been heat-treated in hydrogen for 4 hr. at 1450° C. and this treatment was stated to have reduced the oxygen, present as  $\text{Cr}_2\text{O}_3$ , to less than 0.005% and the nitrogen to below 0.01%.

Owing to the odd shapes of these flakes, accurate specific-resistivity determinations were not possible, but the indications were that the room-temperature resistivity had been decreased by a factor of over 4 as a result of the treatment.

In order to obtain some idea of the rate at which electrodeposited chromium responds to heat-treatment, the following tests were made, in which the chromium sample was immersed for short periods in a gas-heated alumina tube with a closed end. The tube, of about 1-in. bore, was mounted vertically with the open end uppermost and the closed lower end immersed in a gas-heated muffle furnace. The temperature near the base of this tube was kept at about 1500° C. throughout the tests.

Current and potential leads of fine platinum-10% rhodium alloy wires, insulated with refractory tubing, were spot welded to the flake to be investigated, and wired to an alumina rod so that this unit could be quickly moved in and out of the tube.

Preliminary experiments were carried out on a flake of chromium that had been heat-treated for 4 hr. in hydrogen at 1450° C. The room-temperature resistance  $R$  was first measured. The flake was then quickly lowered to the heated end of the tube, held there momentarily, and quickly removed, the whole procedure occupying about 1 sec. The room-temperature resistance was remeasured and found to be 0.98<sub>5</sub>  $R$ . After the experiment had been repeated with a longer immersion so that the total time was 3 sec., the resistance had risen slightly to 0.99  $R$ .

Two conclusions can be drawn from these results. First, the observed fall in resistance after only 1 sec.

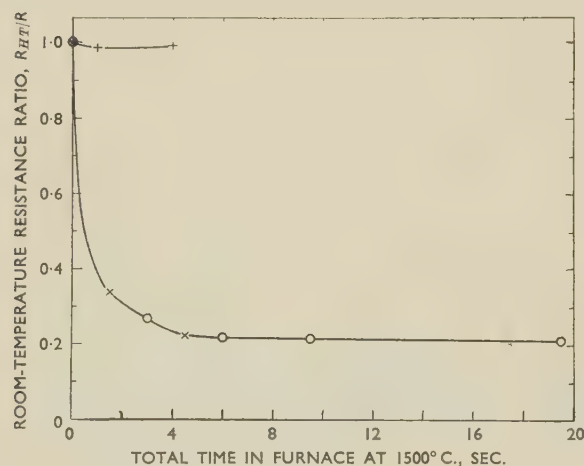


FIG. 1.—Effects of Short Periods in Furnace at 1500° C. on Electrical Resistance of Chromium Flakes.

KEY  
+ Previously heated to 1450° C.  
x As electrodeposited (1st sample).  
o " " (2nd sample).

total time indicates that the time of immersion has been sufficient for the temperature of the sample to exceed the previous heat-treatment temperature of 1450° C. Secondly, the rise in resistance due to oxidation of the

specimen caused by the longer immersion time was small and relatively unimportant.

Similar experiments were then made on two of the freshly deposited flakes, and the results obtained are plotted in Fig. 1. The heat-treatment at 1500° C. is seen

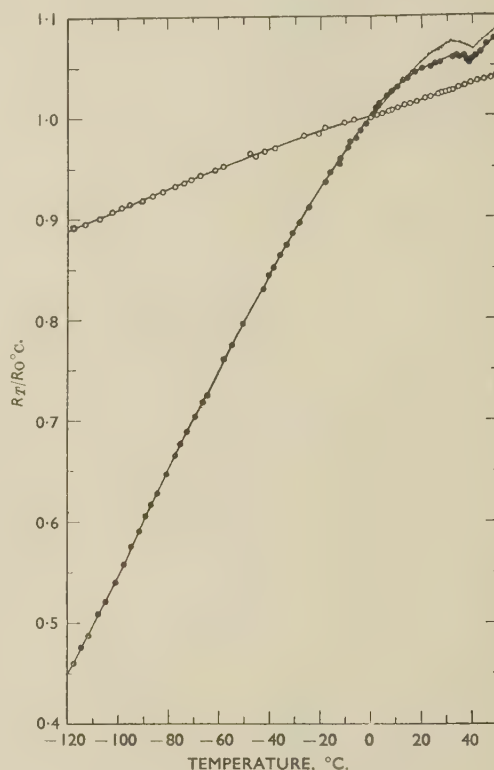


FIG. 2.—Variation with Temperature of Electrical Resistance of Electrodeposited Chromium Flakes.

KEY  
o As electrodeposited.  
• After 4 hr. in hydrogen at 1450° C.  
• " 6 sec. in air at 1470° C.

to cause the resistivity to fall to 0.21 $R$ ; furthermore, the change takes place very quickly and has almost reached completion after only 6 sec.

Resistivity measurements over a temperature range which included the anomalous region were also made on a freshly deposited flake and on flakes that had been heat-treated in hydrogen or in air as described above. These results are reproduced in Fig. 2, where the resistance values are expressed as ratios with respect to the resistance at 0° C. Whereas the anomaly is clearly evident at about 38° C. for the sample heated in hydrogen and at about 40° C. for the sample heated in air, there is no sign of an anomaly in the curve for the freshly deposited sample.

### III.—EXPERIMENTS ON AN ELECTRO-DEPOSITED CHROMIUM TUBE

#### 1. DETAILS OF TUBE

The tube of electrodeposited chromium prepared for the thermal-conductivity investigation was 18.05 cm. in length, 1.28 cm. in external dia., and 0.63 cm. in internal dia. It had been deposited on a copper core, sub-



sequently removed. As deposited, the sample was stated to contain 0.43% oxygen, mostly present as  $\text{Cr}_2\text{O}_3$  and hydrated oxides.

The bore of the tube, which was slightly eccentric at one end, was measured in three directions inclined at  $60^\circ$  to each other to an accuracy of  $\pm 0.0005$  in. over the central 4 in., at intervals of 0.5 in. The external diameter was also measured to comparable accuracy at these positions, and the mean cross-sectional area of the centre portion of the tube was found to be  $0.971 \text{ cm}^2$ , with extreme variations of  $0.006 \text{ cm}^2$ .

When these measurements were repeated after heat-treatment at  $405^\circ \text{C}$ ., the mean internal diameter was found to have decreased by about 0.01 cm. and the mean external diameter by 0.008 cm. These changes are equivalent to a decrease of  $0.0065 \text{ cm}^2$  in the area. The length had decreased from 18.05 to 17.9 cm. After the final heating to  $1410^\circ \text{C}$ ., the outer diameter had decreased by a further  $0.002 \text{ cm}$ .

The initial density was  $6.975 \text{ g./cm}^3$ . After the heat-treatment at  $405^\circ \text{C}$ . this had increased to 7.08 and after that at  $1410^\circ \text{C}$ . to  $7.15 \text{ g./cm}^3$ .

## 2. ORDER OF HEAT-TREATMENT AND EXPERIMENTS

Electrical-resistivity measurements were first made on the tube over the range from the temperature of liquid oxygen to room temperature. Thermal-conductivity and electrical-resistivity determinations were then carried out up to a mean temperature of approximately  $100^\circ \text{C}$ ., after which further resistivity measurements were made to liquid-oxygen temperature.

The tube was then inserted into an alumina tube with a closed end, which could be placed in an electrically wound tubular furnace and heated uniformly to successively higher temperatures with intermediate cooling to room temperature. During the heating and cooling, electrical-resistivity measurements were made and care was taken to start cooling the specimen only when the resistivity had dropped to a steady value at the heat-treatment temperature. The specimen was heat-treated in this manner to mean temperatures of  $170^\circ$ ,  $213^\circ$ ,  $405^\circ$ ,  $545^\circ$ ,  $860^\circ$ ,  $1054^\circ$ , and  $1410^\circ \text{C}$ . After each heat-treatment, electrical-resistivity measurements were made to liquid-oxygen or -nitrogen temperatures and occasionally to liquid-helium temperatures, and thermal-conductivity determinations were made to a mean temperature which did not necessitate taking any part of the working section of the tube above the particular heat-treatment temperature. All treatments and experiments involving temperatures above  $400^\circ \text{C}$ . were carried out under vacuum conditions to minimize oxidation of the specimen.

## 3. TECHNIQUE

In order to make the electrical-resistivity measurements, current leads were attached to the ends of the tube and fine thermocouples of Nichrome/Constantan or platinum/platinum-10% rhodium wires (depending on the temperature to be attained) were spot welded to it at the centre and at approximately 6 cm. from each end. The two outer thermocouples served as potential leads as well as for temperature measurement. The electrical resistivity was obtained by comparison of the potential drop on this section of the specimen with that across a

resistance of known value. All electrical measurements were made on a vernier potentiometer, and to eliminate thermoelectric effects the current through the specimen was reversed and the observations repeated.

For the purpose of measuring the thermal conductivity, the tube, with thermocouples attached, was either soldered to, or made a shrink fit into, one of two rods (depending on the apparatus used) of known conductivity and of slightly larger diameter, and having three equispaced fine thermocouples attached along its length. A heating coil was fixed in the free end of the tube and a water-flow calorimeter to the free end of the standard bar. The composite bar was mounted centrally within a vertical guard tube, with the chromium tube uppermost, and heat-insulating powder was packed into the axial hole of the specimen and into the space between the bar and its surrounding tube. The temperature gradients were obtained from the thermocouple readings, and the heat flow in the chromium tube was derived both from the gradient established in the standard bar and the heat absorbed in the water-flow calorimeter. Above  $400^\circ \text{C}$ . water-cooling was dispensed with and the heat flow derived only from the gradient in the standard bar. A similar low-temperature assembly, but with the position of the test specimen and standard reversed, is shown in an earlier paper<sup>14</sup> and the high-temperature assembly has also been previously illustrated.<sup>15</sup> The thermal conductivity  $\lambda$ , at various mean temperatures was calculated from the above data, and the dimensions of the tube, using  $\lambda = H(L_1 - L_2)/A(T_1 - T_2)$ , where  $H$  is the quantity of heat flowing in the tube of area  $A$ , and maintaining temperatures of  $T_1$  and  $T_2$  at the thermocouple positions  $L_1$  and  $L_2$ .

In evaluating thermal-conductivity and electrical-resistivity data, no allowance has been made for dimensional changes due to change in temperature during the actual experiment.

## 4. EXPERIMENTAL RESULTS

The values obtained from the electrical-resistivity determinations are plotted in Fig. 3, where the range  $0^\circ$ – $60^\circ \text{C}$ ., which includes the anomalous region, is also drawn on an enlarged scale. After heat-treatment to  $545^\circ \text{C}$ ., the anomaly is apparent in the region of  $35^\circ$ – $40^\circ \text{C}$ . and becomes more pronounced with increase in the heat-treatment temperature. There is thus general agreement with the results of Fig. 2 for the electrodeposited flakes of chromium.

The heat-treatment is also seen to have a considerable influence on the actual resistivity value. Dotted lines show the approximate course of the changes on heating to a higher temperature. For each stage the resistivity values are reproducible along the curves represented as full lines.

Two determinations in liquid helium are included in Fig. 3. The value of  $0.215 \text{ microhm cm}^2/\text{cm}$ . was obtained after heat-treatment at  $1054^\circ \text{C}$ ., and after the heat-treatment at  $1410^\circ \text{C}$ . this had decreased to about  $0.05 \text{ microhm cm}^2/\text{cm}$ . The latter value is only some 0.004 of the resistivity at  $0^\circ \text{C}$ . The other value of  $31.65 \text{ microhm cm}^2/\text{cm}$ ., plotted in Fig. 3 as though measured after the heat-treatment at  $170^\circ \text{C}$ ., was actually determined on a second tube of electrodeposited chromium. This tube had not been heat-treated, but

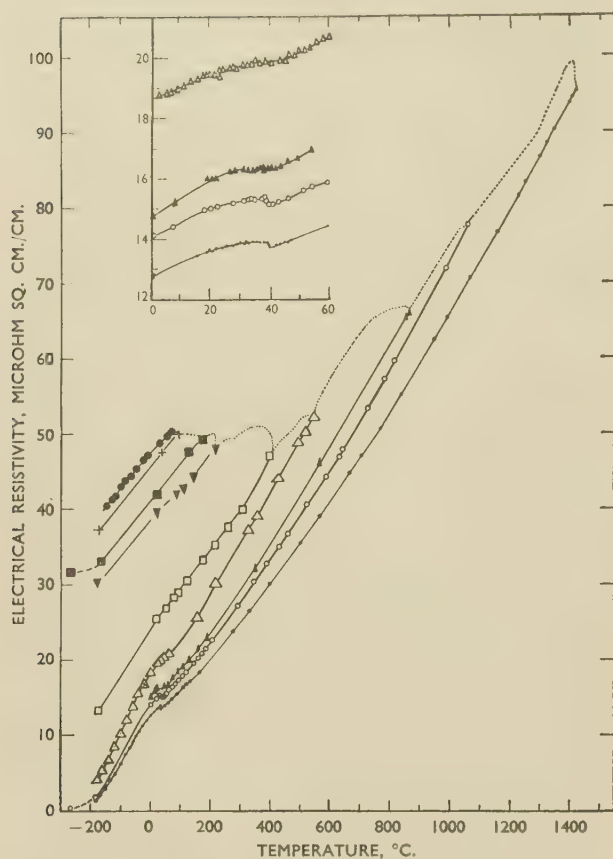


FIG. 3.—Effect of Heat-Treatment on Electrical Resistivity of Electrodeposited Chromium Tube.

KEY TO FIGS. 3 AND 4  
 ● As electrodeposited.  
 After heat-treatment at:  
 + 100° C.    ▽ 213° C.    △ 545° C.    ○ 1054° C.  
 ■ 170° C.    □ 405° C.    ▲ 860° C.    ● 1410° C.

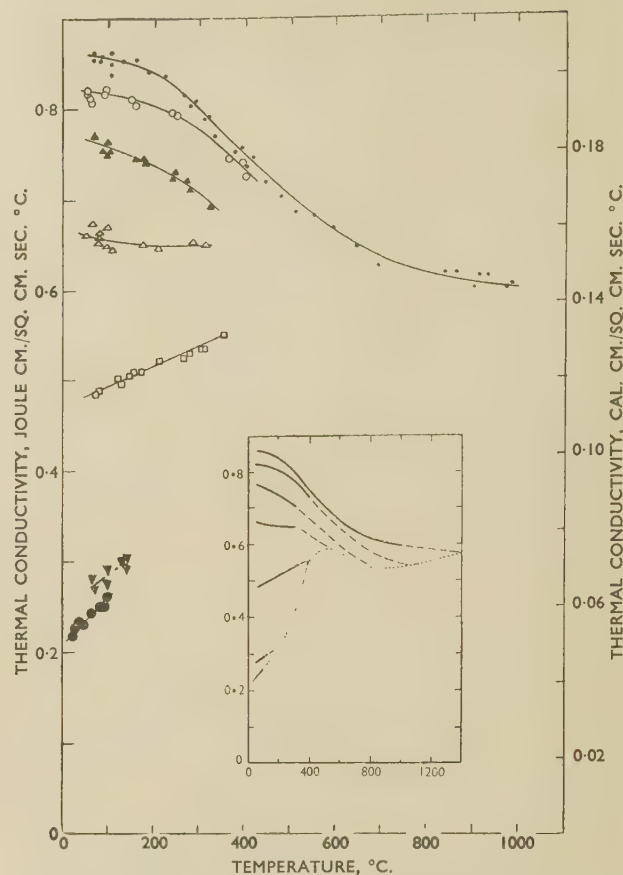


FIG. 4.—Effect of Heat-Treatment on Thermal Conductivity of Electrodeposited Chromium Tube.

KEY TO INSET  
 . . . . . Probable curve on heating.  
 - - - - - Probable curve on cooling or reheating.  
 ————— Experimental curve on cooling or reheating.

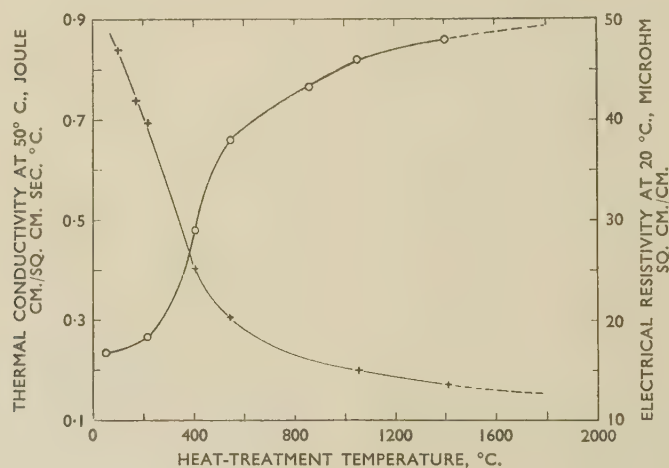


FIG. 5.—Thermal Conductivity (○) at 50° C. and Electrical Resistivity (+) at 20° C. of Electrodeposited Chromium Plotted Against Temperature of Heat-Treatment.



had an initial resistivity of 41.3 microhm cm.<sup>2</sup>/cm. at 0° C., which agreed closely with that of the first tube after heat-treatment at 170° C. In this instance the ratio of the resistivity at -269° C. to that at 0° C. is only 0.765, and the inclusion of this value serves to show the high residual resistivity possessed by the freshly deposited chromium and to emphasize the extent to which this quantity is decreased by heat-treatment. The heat-treatment at 1410° C. has reduced the residual resistivity in the ratio of about 650:1, whereas the resistivity at 0° C. has only been reduced in the ratio of about 3.4:1.

Fig. 4 contains the corresponding results for the thermal conductivity. Full lines have been drawn through the experimental points obtained for each condition. These are reproduced in the inset portion of the figure, where the probable extrapolations to the limit of each heat-treatment are shown by broken lines. The thermal-conductivity values should be reproducible on heating or cooling to these limiting temperatures. A dotted line indicates the probable variation of equilibrium thermal conductivity with temperature for continuous heating beyond the previous heat-treatment temperature and to the upper limit of 1410° C.

Heat-treatment at 1410° C. is seen to cause the thermal conductivity at 50° C., to increase to nearly 3.7 times the initial value. Fig. 5 shows the thermal conductivity at 50° C. and the electrical resistivity at 20° C. plotted against the heat-treatment temperature. From this it appears that the greatest rate of increase in conductivity coincides with heat-treatment at about 400° C.

It also seems likely that heating to above 1410° C. will produce further changes. A thermal conductivity of the order of 0.9 joule cm./cm.<sup>2</sup> sec. °C. is indicated after heat-treatment close to the melting point, whilst the corresponding extrapolated resistivity is 12.5 microhm cm.<sup>2</sup>/cm., a value about 4.5% less than that reported by Adcock<sup>16</sup> for vacuum-melted chromium.

Values of the electrical resistivity and thermal conductivity read from smooth curves drawn through the experimental results are set out in Table II, which also contains values for the Lorenz function, the product of these two quantities divided by the absolute temperature.

#### IV.—DISCUSSION OF RESULTS

The present work confirms that heat-treatment of electrolytic chromium produces large changes in the thermal conductivity. These changes are most marked for heat-treatment in the region of 400° C., the temperature at which Brenner *et al.*<sup>1</sup> consider evolution of hydrogen to become almost complete. The high initial resistivity of electrodeposited chromium was attributed by these workers to the presence of oxygen in the form of oxide, and they regarded the heat-treatment not as a means of removing oxygen but as promoting an agglomeration of the oxide to a condition in which it has a reduced influence on the electrical resistivity and other properties.

In this connection it is interesting to note that the fully heat-treated chromium tube finally attained about the same resistivity as the vacuum-melted metal,<sup>16</sup> and that comparable results were obtained for the flakes of

electrodeposited chromium in which the oxygen content had been reduced by conducting the heat-treatment in an atmosphere of hydrogen.

TABLE II.—*Thermal Conductivity, Electrical Resistivity, and Lorenz Function of a Chromium Tube, as Electrodeposited and after Various Heat-Treatments.*

Condition	Temperature, °C.	Thermal Conductivity, joule cm./cm. <sup>2</sup> sec. °C.	Electrical Resistivity, microhm cm. <sup>2</sup> /cm.	10 <sup>8</sup> × Lorenz Function, joule ohm/sec. °C. °K.
As-deposited	-180	...	39.0	...
	20	...	48.5	...
	50	0.23 <sub>5</sub>	49.8	3.6
	100	0.26	52.0	3.6
After above measurements	-180	...	36.8	...
	20	...	47.0	...
	-180	...	32.2	...
	20	...	42.0	...
After heating to 213° C.	-180	...	30.0	...
	20	...	39.7	...
	50	0.26 <sub>5</sub>	40.7	3.3
	100	0.28 <sub>5</sub>	42.7	3.2 <sub>5</sub>
	150	0.30 <sub>5</sub>	45.0	3.2
After heating to 405° C.	-180	...	13.2	...
	20	...	25.5	...
	50	0.48	26.9	4.0
	150	0.50 <sub>5</sub>	32.0	3.8 <sub>5</sub>
	250	0.52 <sub>5</sub>	37.5	3.8
	350	0.55	43.2	3.7
After heating to 545° C.	-180	...	4.0	...
	20	...	19.3	...
	50	0.66	20.3	4.1 <sub>5</sub>
	150	0.65 <sub>5</sub>	25.4	3.9
	250	0.65	32.2	4.0
	300	0.65	35.8	4.1 <sub>5</sub>
After heating to 860° C.	20	...	16.0	...
	50	0.76 <sub>5</sub>	16.8	3.8
	150	0.75	21.0	3.7
	250	0.72 <sub>5</sub>	26.5	3.6 <sub>5</sub>
	350	0.68 <sub>5</sub>	32.1	3.5 <sub>5</sub>
After heating to 1054° C.	-269	...	0.21 <sub>5</sub>	...
	-180	...	1.8	...
	20	...	15.0	...
	50	0.82	15.6	3.9 <sub>5</sub>
	150	0.81	19.8	3.8
	250	0.79 <sub>5</sub>	25.0	3.8
	350	0.75 <sub>5</sub>	30.6	3.7
	400	0.73	33.5	3.6 <sub>5</sub>
After heating to 1410° C.	-269	...	0.05	...
	-180	...	1.4 <sub>5</sub>	...
	20	...	13.6	...
	50	0.86	14.1	3.7 <sub>5</sub>
	150	0.85	18.0	3.6
	250	0.82 <sub>5</sub>	22.7	3.6
	350	0.77	27.8	3.4 <sub>5</sub>
	400	0.75	30.3	3.4
	500	0.70 <sub>5</sub>	35.7	3.2 <sub>5</sub>
	600	0.66 <sub>5</sub>	41.2	3.1 <sub>5</sub>
	700	0.63 <sub>5</sub>	47.2	3.1
	800	0.61 <sub>5</sub>	53.2	3.0 <sub>5</sub>
	900	0.60 <sub>5</sub>	60.0	3.1
	1000	0.60	66.4	3.1 <sub>5</sub>

Regarding the relation between the electrical resistivity and the thermal conductivity, it will be seen that all the values of the Lorenz function given in the last column

of Table II considerably exceed the theoretical value of  $2.45 \times 10^{-8}$  joule ohm/sec.  $^{\circ}\text{C}.$   $^{\circ}\text{K}.$ , and it is of interest to seek a possible explanation.

The theory assumes both conduction processes to be entirely due to electrons and neglects the contribution that the lattice makes to the thermal conductivity. Such contributions generally tend to become of increasing importance as the temperature and conductivity are reduced. High values for the Lorenz function are then obtained. For some of the principal groups of metals and alloys it has been shown,<sup>14, 17-21</sup> that a fair correlation of the experimental values of thermal conductivity,  $\lambda$ , and electrical resistivity,  $\rho$ , for wide ranges of the absolute temperature,  $T$ , is given by an equation of the form:

$$\lambda = LT/\rho + C \quad (1)$$

where  $L$  is the Lorenz constant (that is, the theoretical value of the Lorenz function) and the constant  $C$  is regarded as the lattice component.

equations, whilst equation (3) indicates a negative value for the lattice component. The explanation is probably associated with a dependence of  $L$  and  $C$ , not only on temperature but also on heat-treatment. This latter possibility militates against the success of a correlation of the results similar to that made in the case of beryllium.<sup>22</sup>

In Fig. 6, however, the experimental points have been plotted in the manner adopted for beryllium and have again been tagged to show the mean temperatures to which they apply. It will be seen that the points for the as-deposited condition and those obtained after heat-treatment to  $213^{\circ}\text{C}.$  lie reasonably close to the lower broken line, which has been drawn to have a slope equal to the theoretical value of the Lorenz constant. The intercept of this line with the axis would indicate values for the lattice component of 0.071 and 0.082 joule cm./cm.<sup>2</sup> sec.  $^{\circ}\text{C}.$  at  $50^{\circ}$  and  $100^{\circ}\text{C}.$ , respectively. Confining attention to the  $50^{\circ}\text{C}.$  points, each heat-treatment at higher temperature is seen to result in an increasing

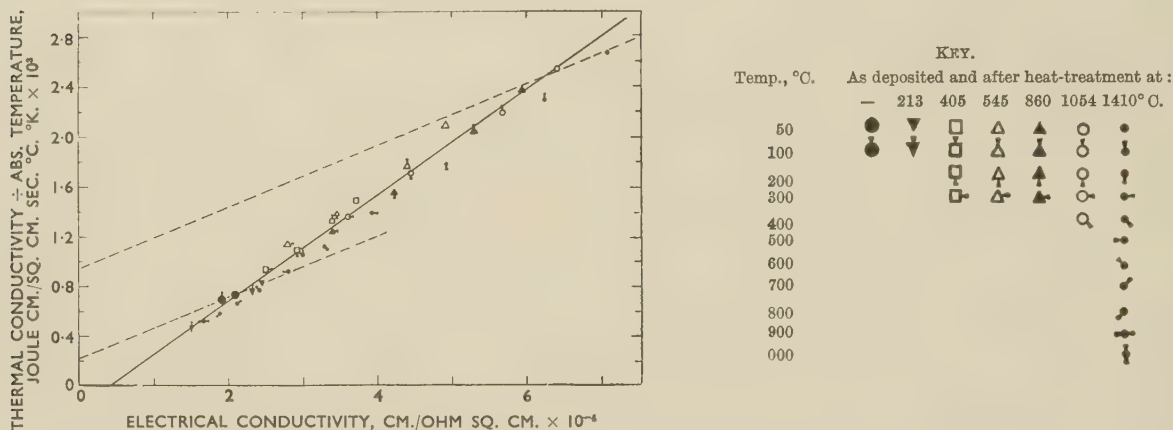


FIG. 6.—Thermal Conductivity Divided by Absolute Temperature of Electrodeposited Chromium Plotted Against Electrical Conductivity for As-Deposited and Heat-Treated States.

When the results of the present investigation are treated in this manner and  $\lambda$  is plotted against  $T/\rho$ , the points all lie within  $\pm 16\%$  of the line:

$$\lambda = 3.6 \times 10^{-8} T/\rho \quad (2)$$

In Fig. 6  $\lambda/T$  is plotted against  $1/\rho$ , and it will be seen that the experimental points now lie within  $\pm 12\%$  of the line:

$$\lambda/T = \frac{4.24 \times 10^{-8}}{\rho} - 0.17 \times 10^{-3} \quad (3)$$

It is suggested that this equation can be used to estimate the thermal conductivity of electrolytic chromium to within this accuracy from observations of the electrical resistivity.

In formulating equation (1) and equating  $L$  to the Lorenz constant and  $C$  to the lattice component, there is an assumption that both quantities are independent of temperature. This equation transforms to equation (2) when the lattice component is zero, and to equation (3) when the lattice component is proportional to the temperature. The theoretical value of the Lorenz constant is seen to be considerably exceeded in both

departure above this broken line, until, after the heat-treatment at  $1054^{\circ}$  and  $1410^{\circ}\text{C}.$  the upper broken line, drawn with the same slope, is reached. This behaviour is consistent with an increase in the lattice component of the thermal conductivity with increase in heat-treatment temperature. The final value of this component at  $50^{\circ}\text{C}.$  is about 0.31 joule cm./cm.<sup>2</sup> sec.  $^{\circ}\text{C}.$ , which is more than four times the initial value.

When the points of Fig. 6 for  $100^{\circ}$ ,  $200^{\circ}$ , and  $300^{\circ}\text{C}.$  are considered in this way, similar tendencies will be observed, but as these temperatures increase a decrease in the value of the lattice component becomes apparent. After heating to  $1410^{\circ}\text{C}.$  the lattice components at  $100^{\circ}$ ,  $200^{\circ}$ , and  $300^{\circ}\text{C}.$  are respectively 0.28, 0.27, and 0.24 joule cm./cm.<sup>2</sup> sec.  $^{\circ}\text{C}.$

It is understandable that both the electronic and the lattice components of thermal conductivity should increase as gaseous impurities and imperfections are removed by heat-treatment and the density of the metal is raised, but the actual values of the lattice component are surprisingly high. On the basis of the foregoing interpretation, the lattice component accounts for about one-third of the thermal conductivity, and the results now obtained for chromium are seen to be comparable,



in this respect, with those previously recorded for beryllium. This is somewhat unexpected, as the characteristic temperature of chromium is considerably less than that of beryllium.

The density of the tube increased by 2.5% as a result of the heat-treatment. The final value of 7.15 g./cm.<sup>3</sup> is consistent with a value of 7.18 g./cm.<sup>3</sup> for the density of chromium if 0.43 wt.-% oxygen is assumed to be present as Cr<sub>2</sub>O<sub>3</sub>. This is still below the theoretical value of 7.20 g./cm.<sup>3</sup>.

With regard to the anomaly, no attempt has so far been made to ascertain whether corresponding changes are detectable in the thermal conductivity, nor is it possible to offer a satisfactory explanation for the phenomenon. Two aspects do, however, arise from the

might be associated with the antiferromagnetic properties of either chromium or chromic oxide. In this connection, however, it seems desirable to draw attention to pronounced differences between the electrical properties of chromium and those of some other antiferromagnetic materials. Resistivity/temperature curves for three such alloys are plotted in Fig. 7, together with measurements made on a flake of electrodeposited chromium that had been heated in air to 1470° C. and for which the resistivity at 0° C. has been adjusted to conform to the value for the tube after final heat-treatment. The chromium curve (A) is a typical one: the usual anomaly occurs at about 40° C., a value which agrees closely with the Curie temperature of chromic oxide (41° C. according to Greenwald<sup>23</sup> and about 35° C. according to the specific-heat measurements by Volger<sup>24</sup>) but two independent sets of careful measurements have shown that there is no very distinctive change in the region of 202° C., reported<sup>25</sup> as the Néel temperature of chromium.

Other curves in Fig. 7 give: (C) the results obtained for an antiferromagnetic manganese-copper alloy, kindly supplied by Dr. R. Street of Sheffield University, for which the Néel temperature had been found to be 125° C.; (D) the results of measurements made by Dr. Street<sup>26</sup> on another sample of 85:15 manganese-copper alloy which had been carefully homogenized to correspond to the face-centred cubic modification and for which the Néel temperature, as determined by neutron diffraction was  $70^\circ \pm 5^\circ$  C.; and (E) the results of Giansoldati and Linde<sup>27</sup> for an alloy of gold-manganese which was shown independently to have a Néel temperature of 227° C.

For all three alloys, a change in the resistance/temperature curve occurs at a temperature which is in close agreement with the Néel temperature. Thus, in the case of each alloy it seems clear that the electrical resistivity is influenced by the antiferromagnetism of the metal, whereas for chromium there seems stronger evidence for the change in resistivity to be associated with the magnetic properties of the contained oxide. If this is so, it might account for the other striking difference between the two sets of curves, namely, that the effect is of opposite sign, in that the resistance of chromium undergoes an increase with decrease in temperature, whereas an enhanced rate of decrease occurs with the other metals. The absence of the anomaly in the freshly deposited chromium could be explained if the dimensional changes of the oxide are absorbed by the porosity and state of strain of the metal.

On the foregoing basis it would be expected that the extent of the anomaly in the heat-treated samples would depend on the amount of oxide present and that oxide-free chromium would exhibit no anomaly. The latter condition has not yet been reached, but the curves plotted in Figs. 2 and 3 do not suggest any direct correlation between the form of anomaly and the amount of oxide present, and it seems that a full and satisfactory explanation must await the results of further investigations.

*Note added in proof.*—Precise determinations of the lattice constant of sintered electrolytic chromium have recently been reported by Straumanis and Weng.<sup>28</sup> Their expansivity curve for chromium shows a slight

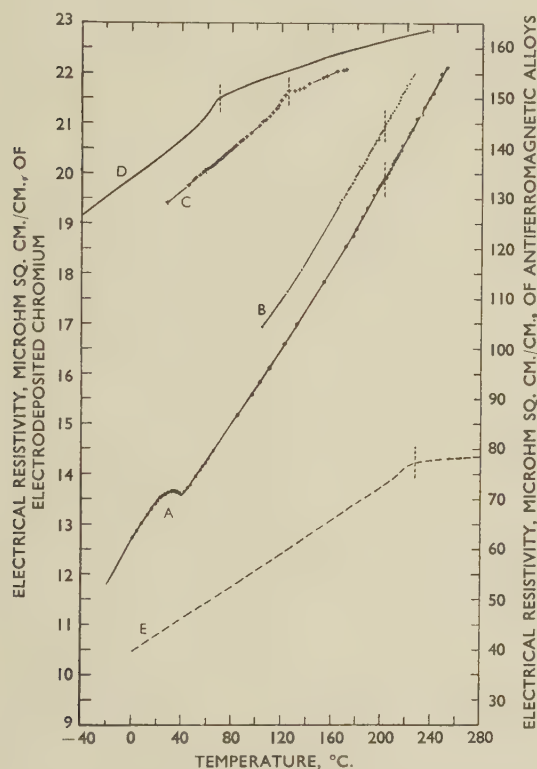


FIG. 7.—Curves of Resistivity Plotted Against Temperature for Electrodeposited Chromium Flake and for Some Antiferromagnetic Alloys.

#### KEY

- Curve A Chromium flake after 6 sec. in air at 1470° C.  
 " B " " " (repeat run).  
 " C 85% manganese-15% copper alloy.  
 " D " " " (face-centred cubic; examined by R. Street<sup>26</sup>).  
 " E Manganese-gold alloy examined by Giansoldati and Linde.<sup>27</sup>  
 : Néel temperature.

electrical-resistivity observations, and consideration of these leads to some tentative suggestions.

The first is the absence of the anomaly in the freshly deposited chromium and its appearance after heat-treatment. This would suggest that some inhibiting action might be attributed to the gaseous impurities or the associated state of strain of the electrodeposited material.

The second relates to the possibility that the anomaly

break at about 32.5° C. The amount of oxygen in their sample was 0.0088 wt.-%.

## ACKNOWLEDGEMENTS

The authors are indebted to Dr. R. Street of Sheffield University for the loan of the sample of manganese-copper alloy and for permission to refer to his results for the completely homogenized sample of this alloy. They are also indebted to Mr. H. E. Bennett of Messrs. Johnson, Matthey and Co., Ltd., for providing the flakes of electrolytic chromium.

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# THE CONSTITUTION OF THE TITANIUM-RICH ALLOYS OF TITANIUM, ALUMINIUM, AND OXYGEN\*

1741

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(Communication from the National Physical Laboratory)

## SYNOPSIS

The constitution of the titanium-aluminium-oxygen alloys containing up to 7.5 wt.-% (12.6 at.-%) aluminium and 1 wt.-% (3 at.-%) oxygen has been determined by microscopical methods up to 1250° C. The  $\alpha$  phase field is stabilized by aluminium and oxygen together to temperatures higher than those estimated from the sum of the effects of the two elements independently considered. The results agree substantially with published work by Van Thyne and Kessler (*Trans. Amer. Inst. Min. Met. Eng.*, 1954, **200**, 193).

## I.—INTRODUCTION

ALUMINIUM is the only known metallic element which significantly raises the transition temperature of titanium and consequently stabilizes the  $\alpha$  phase at higher temperatures. Because of its stabilizing effect on the  $\alpha$  phase, its favourable influence on the mechanical properties, and its low specific gravity, aluminium is used as an alloying constituent in some commercial alloys. Increase in the aluminium content above 8-10%, ‡ however, results in difficulty in working the alloys and in brittleness; consequently, commercial alloys are at present limited to a content of about 5%.

In all commercial titanium alloys, the presence of the interstitially soluble elements, oxygen, nitrogen, hydrogen, and carbon, is important because of their marked effect on the mechanical properties. Since oxygen is the most likely of these elements to be present in titanium in significant amounts, it was decided to investigate its effect on the transition temperature of the titanium-aluminium alloys. The range of compositions investigated, namely, up to 7.5% aluminium and 1% oxygen, adequately covers those likely to be of commercial importance and provides a basis for a study of the mechanical properties of the alloys which is in progress.

Partial or complete investigations of the constitution of the binary titanium-aluminium alloys have been carried out by Duwez and Taylor,<sup>1</sup> Bumps, Kessler, and Hansen,<sup>2</sup> Ogden, Maykuth, Finlay, and Jaffee,<sup>3</sup> and McQuillan.<sup>4</sup> The constitution of the binary titanium-oxygen alloys has been determined by Bumps, Kessler, and Hansen,<sup>5</sup> and by Schofield and Bacon.<sup>6</sup>

Before the work now described was completed, a paper concerned with the same subject, and also with the effects of nitrogen and carbon on the constitution of the titanium-aluminium alloys, was published in the United States.<sup>7</sup> The results of the present investigation substantially confirm those of the American work.

## II.—EXPERIMENTAL METHODS

### 1. MATERIALS

The alloys were prepared from iodide titanium manufactured by the New Jersey Zinc Co., Ltd., high-purity aluminium, and pure  $\text{TiO}_2$ . The titanium had the following average analysis: oxygen 0.02, hydrogen 0.02, nitrogen <0.005, iron 0.016, manganese 0.012, zirconium 0.01, aluminium 0.005, silicon 0.005, vanadium 0.005, lead 0.002 wt.-%. The aluminium had a purity of 99.95 wt.-%. An analysis of the  $\text{TiO}_2$  gave the following results: silicon 0.065, iron 0.03, magnesium 0.05, nickel 0.0001, sodium 0.01, phosphorus 0.10, sulphur 0.035, carbon 0.03, nitrogen 0.6, loss on ignition (mostly water) 0.8%.

### 2. PREPARATION OF ALLOYS

The requisite amounts of titanium and aluminium, or of titanium, aluminium, and compacted  $\text{TiO}_2$ , for each 50-g. ingot were melted together under a reduced pressure of argon (99.8%) in a small arc furnace. Part of the titanium charge was melted first, and the aluminium and  $\text{TiO}_2$  melted into the molten pool. To ensure homogeneity, each ingot was melted four times, being turned over after each of the first three operations. The weights of the buttons agreed closely with the weights of the charges.

### 3. HEAT-TREATMENT

All alloys were separately homogenized at 1200°-1300° C. for 1 hr. or at 1100° C. for 4 hr. in vacuum and water-quenched before subsequent heat-treatment. The homogenizing treatment was carried out in a vertical, platinum-wound resistance furnace. Each specimen was enclosed in a commercially pure titanium crucible suspended by means of a molybdenum wire from a short length of resistance wire in the furnace head. Before quenching, the furnace was filled with argon at atmospheric pressure; a plate was then removed from the

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‡ In the text aluminium and oxygen contents are expressed as wt.-%.

lower end of the furnace tube, and quenching was effected by fusing the wire, thus causing the crucible and contents to fall into a vessel containing water placed under the opened end of the furnace. The same method was used for the determination of phase boundaries at temperatures above 1150° C. The accuracy of temperature control was within  $\pm 3^\circ$  C.

At a later stage in the investigation, it was found that some of the specimens contained significant amounts of hydrogen (about 0.03 wt.-% (1.5 at.-%)) which resulted in duplex structures even after heat-treatment at temperatures well below the transformation temperature of titanium (Fig. 1, Plate XXXVII). Before carrying out heat-treatments for determining the position of the phase boundaries, the homogenized material was therefore reheated for 4 hr. at 900° C. in vacuum and furnace-cooled. This treatment reduced the hydrogen to about 0.01 wt.-% (0.5 at.-%) and was sufficient to prevent the occurrence of the duplex structures (Fig. 2, Plate XXXVII). That these structures were associated with hydrogen content was confirmed by reheating a vacuum-treated specimen which showed a single-phase microstructure in a small sealed silica tube containing hydrogen, after which the duplex structure reappeared.

For the determination of the position of the phase boundaries below 1150° C., each vacuum-treated specimen was wrapped in a single thickness of molybdenum foil and sealed in an evacuated silica tube. After heat-treatment in a tubular electric-resistance furnace, controlled to  $\pm 2^\circ$  C., the tube was simultaneously immersed in water and broken. The temperatures and corresponding times were as follows:

Temp., ° C.	Time, hr.
880-975	24
1000-1075	16
1100-1150	6
1150-1200	3
1200-1300	1

It has been suggested by McQuillan<sup>8</sup> that a delay in quenching from temperatures near the  $\beta/(\alpha + \beta)$  boundary, such as may occur during quenching from sealed silica tubes, results in some alloys in  $\alpha$  precipitates which are indistinguishable from equilibrium  $\alpha$ . To check this point, two specimens of an alloy containing 1% aluminium and 0.5% oxygen were sealed in separate silica tubes and heated together for 16 hr. at 1000° C., a temperature considered to be just below the upper boundary of the  $(\alpha + \beta)$  phase field. One tube was then quickly withdrawn from the furnace and broken under water, the whole operation taking approximately 2 sec. The other was then withdrawn and allowed to remain for 5 sec. in air before the tube was plunged into water and broken. The microstructures of sections of the two specimens were very similar. The only difference between them appeared to be that in the specimen held longer before quenching, the "transformed  $\beta$ " was slightly coarser. It may be argued that the material was in the  $\beta$  field before quenching and that  $\alpha$  precipitates had been formed during the 2 seconds' delay. If this were the case, then it seems very unlikely that a further 5 seconds' delay would not have resulted in further precipitation of  $\alpha$ .

In another experiment, two specimens of the same alloy were placed together inside a modified Rosenhain

quenching apparatus,<sup>9</sup> one being enclosed in a small silica tube of dimensions similar to those normally used for heat-treatment, except that one end of the tube was open. Both specimens were wrapped round with a few turns of fine molybdenum wire to prevent direct contact with the silica. The small silica tube was secured to one end of a fine molybdenum wire, the other end of the wire being attached to a steel rod working through a Wilson seal. The specimens, which had originally been homogenized at 1100° C. and then heated at 850° C. in a vacuum to remove hydrogen, were heated at 1050° C. for  $\frac{1}{4}$  hr., the temperature being then reduced to 1020° C. (i.e. about 10° C. above the  $\beta/(\alpha + \beta)$  boundary for a similar period. The silica tube containing one of the specimens was then withdrawn into a cold part of the furnace by operating the rod passing through the Wilson seal, the other specimen remaining meanwhile in the hot part of the furnace. After a lapse of 5 sec., the water was turned on and the whole apparatus, initially under a vacuum, was filled with water, the specimens being washed from the furnace tube into a large flask. In this manner one specimen was drastically quenched instantaneously and the other quenched with approximately 5 seconds' delay from just above the  $\beta/(\alpha + \beta)$  boundary. The respective microstructures are shown in Figs. 3 and 4 (Plate XXXVII). The drastically quenched specimen exhibited fine "transformed  $\beta$ " and the delayed-quench specimen coarse "transformed  $\beta$ ", but no particles similar to equilibrium  $\alpha$ , as shown in Fig. 6 (Plate XXXVII), were present.

#### 4. MICROSCOPICAL EXAMINATION

The preparation of specimens for microscopical examination calls for no special comment except that those low in oxygen (0.05%) were difficult to polish. Final polishing of these specimens was carried out on a rotating pad of Selvyt-type material, using water and  $\gamma$ -alumina. Other specimens were finished with chromic oxide instead of  $\gamma$ -alumina. All specimens were etched in an aqueous solution containing 0.5% hydrofluoric acid and 1.0% nitric acid.

#### 5. ANALYSIS

The aluminium content of all the alloys was determined on homogenized material and agreed with the nominal content to within  $\pm 2\%$ . The gas content of two alloys was determined by vacuum-fusion, with the following results:

Nominal wt.-%		Actual wt.-%			
Aluminium	Oxygen	Aluminium	Oxygen	Nitrogen	Hydrogen
2.5	0.03	2.50	0.05	0.01	0.02
7.5	0.5	7.62	0.45	0.06	0.025

In constructing the equilibrium diagrams, the nominal percentages of both aluminium and oxygen have been used.

### III.—DISCUSSION OF RESULTS

The effects of aluminium up to 7.5% and of oxygen up to 1% on the transition point of titanium and on the extent of the  $(\alpha + \beta)$  phase field are illustrated in Fig. 7 (a)-(c). The effect of oxygen alone on the transition



point has been taken from the results of previous work.<sup>6</sup> The present results agree substantially with published work by Van Thyne and Kessler,<sup>7</sup> as shown by values (indicated by crosses in Fig. 7) taken from their diagrams; the boundaries are, however, more closely bracketed and the  $(\alpha + \beta)/\beta$  boundary has been determined at greater aluminium contents than in the American work. The higher transition temperatures obtained in the present work in alloys containing nominally 0.05% oxygen may be explained on the assumption that the corresponding alloys in the American work (designated 0% oxygen) have slightly lower oxygen

elements considered separately; for example, the transition temperature of an alloy containing 7.5% aluminium and 1% oxygen is about 228° C. above that of titanium, whereas it would be about 140° C. if the sum of the effects of the two elements were independently considered.

#### ACKNOWLEDGEMENTS

The work described above has been carried out as part of the General Research Programme of the National Physical Laboratory and this paper is published by permission of the Director of the Laboratory.

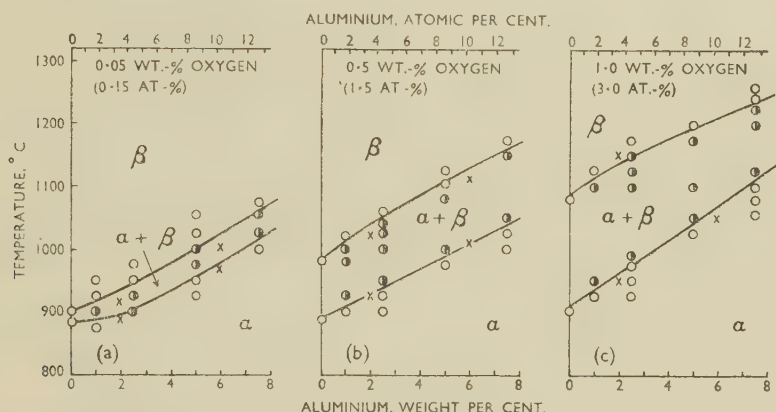


FIG. 7.—Effects of (a) 0.05 wt.-%, (b) 0.5 wt.-%, and (c) 1.0 wt.-% Oxygen on the Transition Temperature of Titanium-Aluminium Alloys Containing up to 7.5 wt.-% Aluminium.

x Results of Van Thyne and Kessler.<sup>7</sup>

contents. The form of the “transformed  $\beta$ ” phase depends on the oxygen content, as well as on the severity of the quench, as in pure titanium-oxygen alloys. On quenching alloys with low oxygen contents from sealed silica tubes, the transformed  $\beta$  appears as serrated grains, with traces of Widmanstätten structure sometimes faintly visible (Fig. 5, Plate XXXVII). The transformed  $\beta$  in the  $(\alpha + \beta)$  microstructure of specimens low in oxygen is also difficult to resolve. As the oxygen content is increased the more usual Widmanstätten (basket-weave) structure appears (Fig. 6, Plate XXXVII).

Ternary isothermal sections\* at 950°, 1000°, and 1050° C., constructed from the data obtained, show that with rise in temperature the extent of the  $\beta$  and  $(\alpha + \beta)$  phase fields is increased and that of the  $\alpha$  field correspondingly decreased. A given atomic percentage of oxygen is much more effective in raising the transition temperature and increasing the extent of the  $(\alpha + \beta)$  phase field than is a similar percentage of aluminium. When both aluminium and oxygen are present, the extent to which the transition temperature is raised is much greater than the sum of the effects of the two

The authors wish to acknowledge the assistance given by their colleagues in the Chemistry Section of the Metallurgy Division. The aluminium and vacuum-fusion analyses were carried out, respectively, by Mr. W. S. Stawpert and Mr. C. A. Harvey. Mr. E. H. Lings assisted with the heat-treatment and polishing of some of the specimens.

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# DETERMINATION OF THE SURFACE TENSIONS OF MOLTEN LEAD, TIN, AND INDIUM BY AN IMPROVED CAPILLARY METHOD \*

1742

By D. A. MELFORD,† M.A., Ph.D., MEMBER, and T. P. HOAR,‡ M.A., Ph.D.,  
B.Sc., F.R.I.C., F.I.M., MEMBER

## SYNOPSIS

An improved capillary method for the measurement of the surface tension of molten metals up to  $c. 1000^{\circ}\text{C}$ . is described. Molten metal is forced by measured differential gas (hydrogen) pressure to equivalent levels in two fused silica capillaries of different bore. The contact angle  $\theta$  is not simultaneously determined, but by other measurements is shown to be  $>170^{\circ}$  for lead, tin, and indium, so that  $\cos \theta$  may be taken as  $-1$  with little error. An analysis of the errors of the method is given in an Appendix.

The surface tensions  $\gamma$  of lead, tin, and indium at temperature  $T^{\circ}\text{K}$ . from the m.p. to a few hundred  $^{\circ}\text{C}$ . above it, as determined by the method, are given by

$$\begin{aligned}\gamma_{\text{Pb}} &= 624 - 0.247T \text{ dynes/cm.} & \gamma_{\text{Pb}_{327^{\circ}\text{C}}} &= 480 \text{ dynes/cm.} \\ \gamma_{\text{Sn}} &= 599 - 0.065T \text{ dynes/cm.} & \gamma_{\text{Sn}_{282^{\circ}\text{C}}} &= 566 \text{ dynes/cm.} \\ \gamma_{\text{In}} &= 602 - 0.107T \text{ dynes/cm.} & \gamma_{\text{In}_{156^{\circ}\text{C}}} &= 559 \text{ dynes/cm.}\end{aligned}$$

These values are critically compared with previous experimental and estimated values.

The results lead to molar surface enthalpies (assuming the surface to be a monolayer of atoms) of  $c. 9600$  cal. for lead,  $8500$  for tin, and  $8300$  for indium, and molar surface entropies of, respectively,  $c. 3.3$ ,  $0.4$ , and  $0.8$  cal./ $^{\circ}\text{K}$ .; these values are slightly temperature dependent, leading to positive values of the molar surface heat capacity in each case. They are compared to bulk thermodynamic magnitudes in a discussion of surface bonding and mobility.

## I.—INTRODUCTION

THE recent growth of interest in the properties of liquid metals from the practical aspect has been paralleled by a growing realization that metals afford especially fruitful examples for the examination of theories of the liquid state. Nevertheless, as indicated in recent reviews,<sup>1,2</sup> there are as yet very few reliable and accurate data of so fundamental a property as the surface tension of metals.

A major reason for the lack of good data of metal surface tensions has been the difficulty of devising reliable techniques for measurement. Recently, however, Baes and Kellogg<sup>3</sup> have applied a modified sessile-drop method to the determination of the surface tension of copper, Taylor<sup>4</sup> has improved the maximum-bubble-pressure method for the determination of that of sodium, and Atterton and Hoar<sup>5,6</sup> have devised a new method based on conical capillaries for the determination of that of tin. This last method, although giving in principle a simultaneous determination of surface tension and contact angle, is at present somewhat tedious both experimentally and in computation. We have consequently attempted to improve the conventional cylindrical-capillary method as reported in this paper, and have used the improved technique for the determination of the

surface tensions of lead, tin, and indium over a range of temperatures.

## II.—EXPERIMENTAL TECHNIQUE AND RESULTS

### 1. PRINCIPLE OF THE METHOD

Two fused-silica capillaries of different bore diameters are mounted vertically with their lower ends approximately level. Each capillary contains a molybdenum contact wire, initially protruding from its end. Molten metal is brought to temperature in a crucible below the capillaries and wires, all being in an atmosphere of hydrogen. The wires are then individually adjusted so that, on lowering together, they make contact simultaneously (as indicated electrically) with the surface of the melt. They are then withdrawn, with no relative movement, a distance of  $3\text{--}4$  mm. back into the capillaries, and the wire in the larger capillary is further withdrawn individually by an amount equal to the calculated meniscus correction (see Appendix, p. 204). The capillaries and wires are then immersed in the melt to a depth of approximately  $2$  cm. The gas pressure in each capillary is very slowly reduced until metal enters and

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makes contact with the molybdenum wire, the pressure difference between crucible and capillary when this occurs being measured on a silicone manometer. The difference between the pressures required to force metal into and up to the same level (corrected for the meniscus effect) in two capillaries is thus obtained, and we have (see Appendix)

$$\gamma \cos \theta = -\frac{g\rho_s(h_1 - h_2)}{2(1/r_1 - 1/r_2)},$$

where  $\gamma$  dynes/cm. is the surface tension,  $\theta$  the contact angle between the liquid metal and the capillary wall,  $\rho_s$  g./cm.<sup>3</sup> the density of the manometer fluid, and  $h_1$ ,  $h_2$  cm. are the height differences in the manometer corresponding to contact respectively in the larger and smaller capillaries of radii  $r_1$ ,  $r_2$  cm. As shown later,  $\theta$  is usually well over  $170^\circ$ , so that  $\cos \theta$  can be taken as  $-1$  with very little error.

## 2. APPARATUS

Fig. 1 is a vertical cross-section of the details of the furnace head designed to meet the requirements of the

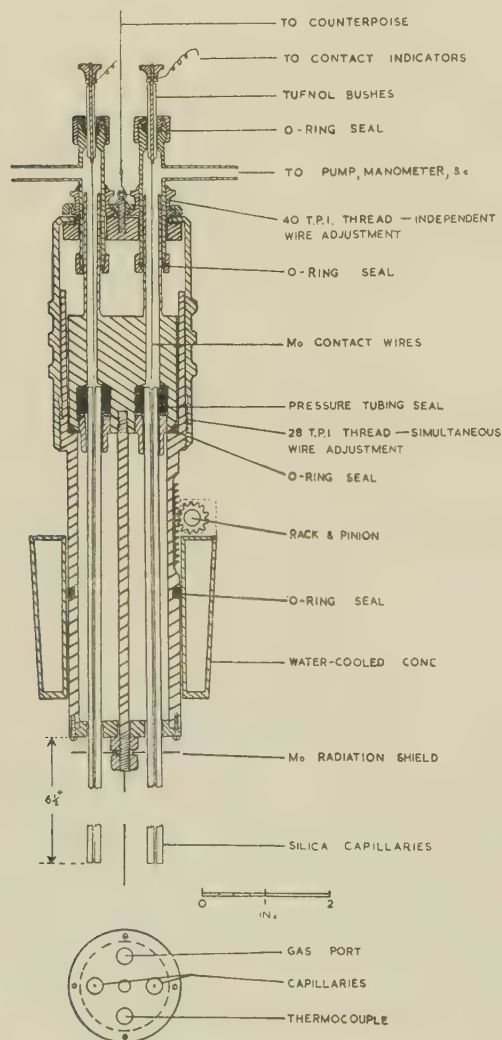


FIG. 1.—Cross-Section of Furnace Head.

method outlined above. The silica capillaries (Thermal Syndicate, Ltd.) are sealed into a cylindrical brass block by means of short sections of rubber pressure-tubing

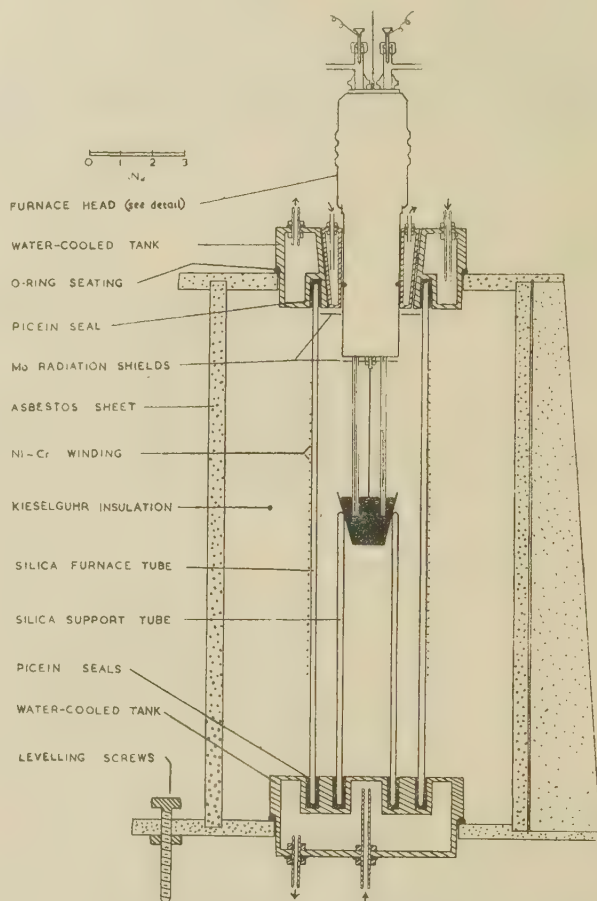


FIG. 2.—Experimental Furnace.

compressed by nuts and washers. This block is in turn sealed into a brass cylinder, which passes through the demountable water-cooled cone fitting into the top of the furnace. Screw-threads provide means of obtaining the required degree of fine adjustment of the contact wires. Rotation of the knurled rings immediately above the furnace head cap provides the individual adjustments, while rotation of the cap itself moves the wires together without relative movement. A rack-and-pinion movement is provided for raising and lowering the capillaries and thermocouple.

The furnace itself is shown in cross-section in Fig. 2. It consists of a 3-in.-dia. silica tube glazed inside and out, wound with "Brightray C" resistance wire and mounted vertically, with the ends sealed into water-cooled brass tanks by means of Picein wax. The fused-silica crucible containing the metal under investigation rests in the end of a silica support tube mounted concentrically with the furnace tube. Kieselguhr, loosely packed around the central tube, provides insulation and increases the thermal capacity of the furnace considerably, hence improving its stability at temperature. Temperature can be controlled and held steady within the accuracy with which it can be measured simply by varying the power input.



Temperature measurement is by means of a Chromel/Alumel thermocouple with its hot junction mounted level with the average position of the ends of the contact wires and approximately 1 cm. from each capillary, feeding a millivoltmeter calibrated over the range  $0^{\circ}$ – $960^{\circ}$  C.

Pressure measurement in the whole system from *c.* 76 cm. of mercury down to  $10^{-1}$  cm. is made by a mercury manometer, from  $10^{-1}$  to  $10^{-4}$  cm. by a McLeod-type (Edwards "Vacustat") gauge, and below  $10^{-4}$  cm. by an ion gauge.

The pressure difference required to force metal into the capillaries is measured by means of a manometer utilizing silicone DC 703 as fluid. This has density 1.075 g./cm.<sup>3</sup> and vapour pressure  $<10^{-10}$  cm. of mercury at the ambient temperature of the experiments ( $17^{\circ} \pm 2^{\circ}$  C.); it is less viscous than butyl phthalate. Fine control of the

and through the molten metal for periods of 8–10 hr. without any sign of contamination occurring.

### 3. EXPERIMENTAL PROCEDURE

The capillaries were received broken into 1-ft. lengths and were used almost without further preparation. Any attempt to grind the ends results in chipping the edge of the capillary mouth; in the "as-broken" condition, the edge is perfectly sharp, and in general the plane of the fracture is perpendicular to the longitudinal axis of the capillary to within  $\pm 2^{\circ}$ .

Two capillaries of the required sizes, with major and minor bore diameters differing by  $\geq 5\%$  of their mean, were selected; the bore-mouth diameters were measured with the aid of a microscope having a micrometer gauge

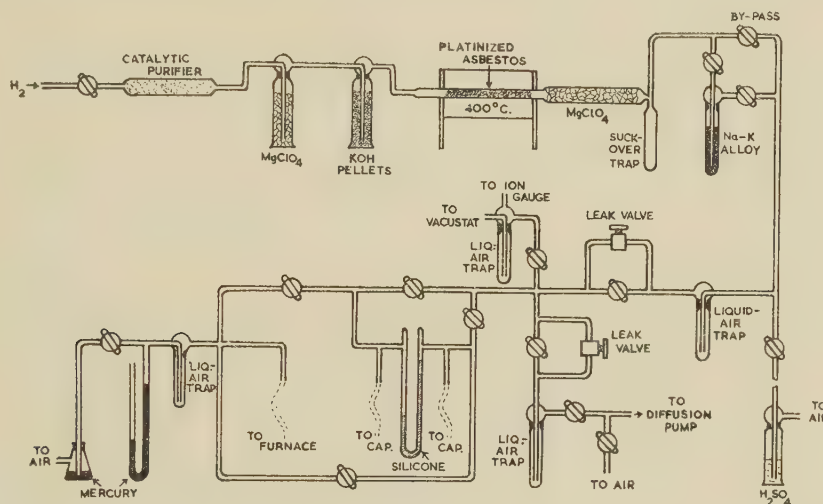


Fig. 3.—Gas Train and Vacuum System.

pressure, essential for the accurate measurement of small pressure differences, is obtained by the use of needle leak valves.

The pumping unit consists of an Edwards  $1\frac{1}{2}$ -in. oil-diffusion pump backed by a two-stage rotary pump. The overall pumping speed is 6–7 l./sec., and the best vacuum obtainable in the somewhat complex system is of the order of  $4 \times 10^{-5}$  cm. of mercury with a leak rate of less than  $3 \times 10^{-5}$  cm./min.

Power for the contact indication circuits is provided by a 2-V. accumulator in series with a 500- $\omega$  resistance. Two 0–5 m.a. milliammeters act as contact indicators.

The gas train for the necessary rigorous purification of hydrogen and the vacuum system are illustrated schematically in Fig. 3. Cylinder hydrogen passes first through a cartridge-type "Deoxo" catalytic purifier (Baker Platinum, Ltd.), is dried with magnesium perchlorate, and thence passes over pure potassium hydroxide pellets and through a furnace held at  $400^{\circ}$  C. containing platinized asbestos (Johnson, Matthey and Co., Ltd.). It is then again dried with magnesium perchlorate and is bubbled through liquid 70:30 sodium–potassium alloy at room temperature, and thence through a liquid-air trap to the experimental furnace. With this arrangement it is possible to blow hydrogen down the capillaries

reading to 0.0001 cm. fitted in the focal plane of the eye-piece. To remove traces of dust and packing materials from the bores, distilled water was drawn through each by means of a filter pump for a few minutes, the flow being frequently interrupted to provide the maximum scouring effect. The capillaries were then flame-dried and fitted into the furnace head, and the molybdenum contact wires, carefully abraded and degreased with re-distilled ether, were inserted. The outside of the capillaries, thermocouple sheath, radiation shield, &c., were degreased, and the metal to be melted was inserted in the crucible. The furnace was closed, evacuated down to a pressure of  $10^{-4}$  cm. of mercury, and allowed to outgas for a minimum of 12 hr. Evacuation was then repeated; a pressure of the order of  $4 \times 10^{-5}$  cm. of mercury, with a leak rate of  $\geq 3 \times 10^{-5}$  cm./min., was regarded as satisfactory.

The gas-train furnace was now switched on and hydrogen passed for 1 hr.; the by-pass was then closed and the circuit through the sodium–potassium alloy opened. Meanwhile the main furnace was switched on and outgassed at temperature for 1–2 hr. It was then isolated from the pumping system and flushed out several times with hydrogen while being brought to the precise temperature required for the first determination. The

furnace pressure was then adjusted to 55–60 cm. of mercury, and the levelling of the contact wires carried out. The small correction (see Appendix) to the height of the wire in the larger capillary was made with the aid of a dial-gauge bearing on its terminal at the top.

The capillaries were then immersed in the melt to a depth of 1–2 cm., and when thermal equilibrium had become established, measurements were begun. One arm of the silicone manometer was connected to the main

was brought into thermal equilibrium at the next temperature.

It will be noted that a fresh metal surface was used for each reading. However, the same silica surface was continually re-immersed. Any form of contamination—for example, metal oxide—liable to affect the silica was thus additive in its effects. A usual first symptom of contamination during the course of an experiment was a sudden increase in the pressure needed to blow hydrogen

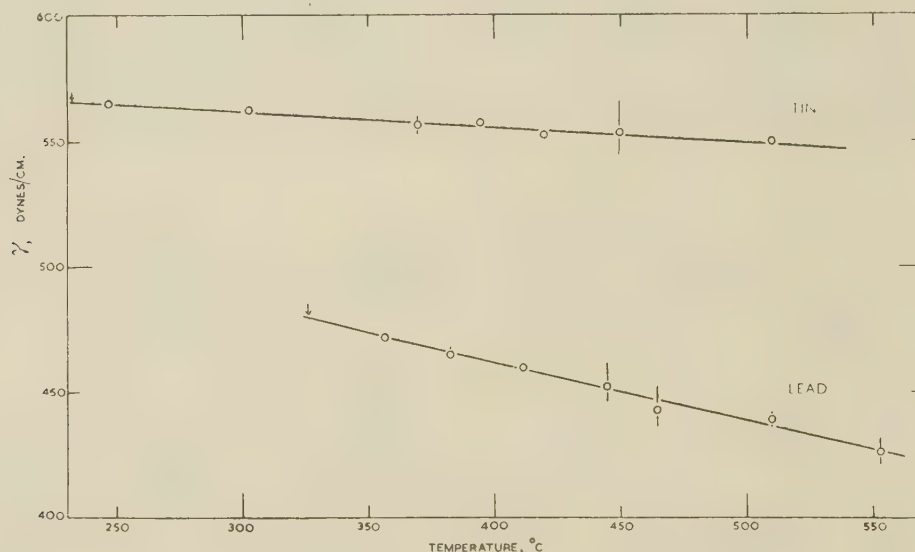


FIG. 4.—Surface Tension of Lead and Tin.

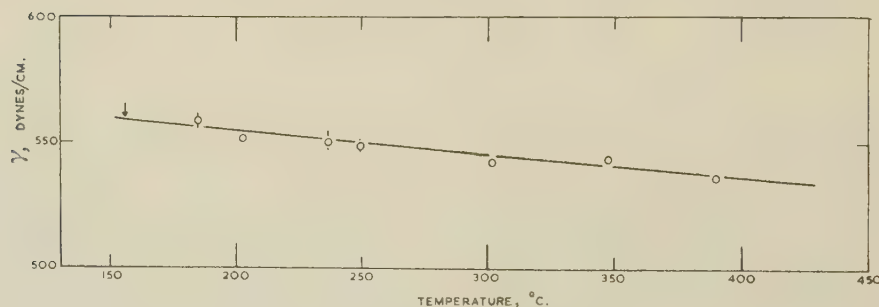


FIG. 5.—Surface Tension of Indium.

gas space in the furnace, the other being connected in turn to each capillary. The pressure in the capillary was slowly reduced by evacuation via the leak valve, until the relevant indicator showed that the metal had entered and made contact with the molybdenum wire. The manometer tap was then closed and both arms of the manometer read. After each reading, metal was blown out of the capillary and hydrogen bubbled through the melt before the process was repeated. Readings were continued at one temperature until two or three concordant results, differing by no more than 1% of their mean, were obtained; five or more readings were often made, and identical values were frequently found. The capillaries were then withdrawn from the melt, and the furnace evacuated and re-filled with hydrogen while it

from the capillary through the melt. This was caused by beads of metal that had adhered to the capillary walls, forming lenses that were forced up past the tip of the contact wire by the next pressure application, thus creating a gas lock. Also, any partial wetting of the capillaries by the metal led to much lower values for the differential pressure required to force metal in and into contact with the wire. Thus when, say, 35–40 determinations were made in the course of an experiment lasting 8–10 hr. without any sign of this erratic behaviour, the conditions were regarded as having been very reliable.

The mathematics of the method and the meniscus correction, and an analysis of the various errors, are given in an Appendix (p. 204).



## 4. MATERIALS

Lead of 99.998% purity was obtained from Johnson, Matthey and Co., Ltd. The impurities, as determined spectrographically, were: Cd 0.001, Cu 0.0005, Ag 0.0005, Bi 0.0003%.

Tin of 99.998% purity was obtained from the same source. The impurities were: Fe 0.001, Cu 0.0003, Bi <0.0002, Pb <0.00015%.

Indium of 99.95% purity was kindly presented by Henry Gardner and Co., Ltd. The impurities were: Sn 0.015, Pb 0.014, Ni 0.002, Fe 0.001, Cd <0.001, Cu <0.001%.

## 5. RESULTS

Figs. 4 and 5 show results for lead, tin, and indium obtained in several different experiments. The vertical lines through the experimental points indicate the limits

metric cross-section lit from below. Readings of the coordinates of the meniscus of the ingot surface were taken; Fig. 6 shows the results for typical ingots of lead, tin, and indium. The value of the contact angle may be obtained from these readings, to within  $\pm 1^\circ$ , by drawing a circular arc through the points and constructing a tangent to it at the point of intersection with the datum axis. In some cases there is a deviation of the experimental points near the point of intersection with the datum axis (Fig. 6); this, if taken into account, leads to a higher value for the contact angle, but for setting a lower limit for the contact angle, no weight has been attached to these points. The contraction of the metal on solidification, causing a sag in the surface, may have caused a decrease in the contact angle—that measured is, in fact, a slightly “receding” angle.

Nevertheless, the angles as measured were  $170^\circ$  for

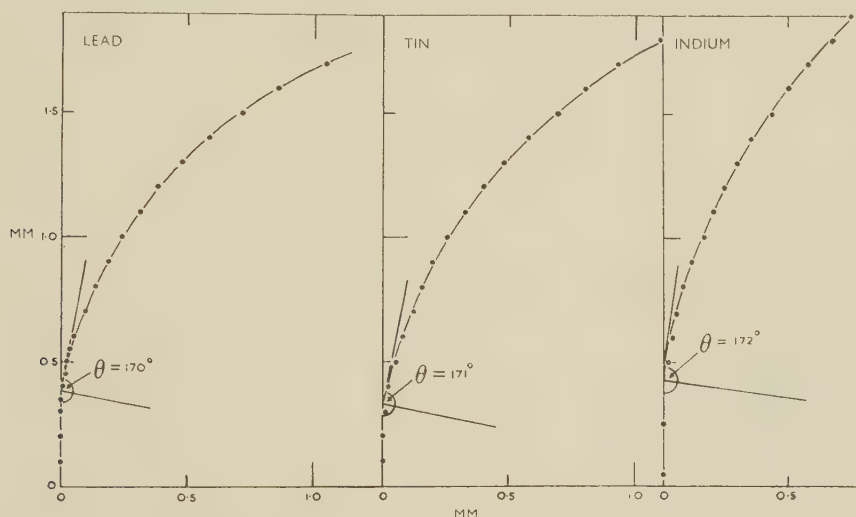


FIG. 6.—Profiles of Solidified Ingots and Determination of Lower Limit of Contact Angle for Lead, Tin, and Indium.

of  $-\gamma \cos \theta$  as calculated from individual experimental readings at temperature  $T$ . Straight lines through the experimental points represent the  $-\gamma \cos \theta/T$  relations for each metal. Since, as shown below,  $\theta$  is  $>170^\circ$ – $172^\circ$ ,  $\cos \theta \sim -1$ , and the straight lines may be taken with very little error as  $\gamma/T$  relationships. We thus find (dynes/cm.)

$$\begin{aligned}\gamma_{\text{Pb}} &= 624 - 0.24 T & \gamma_{\text{Pb}_{327^\circ \text{C}}} &= 480. \\ \gamma_{\text{Sn}} &= 599 - 0.065 T & \gamma_{\text{Sn}_{232^\circ \text{C}}} &= 566. \\ \gamma_{\text{In}} &= 602 - 0.10 T & \gamma_{\text{In}_{156^\circ \text{C}}} &= 599.\end{aligned}$$

The solidified metal ingots removed from the fused-silica crucibles after cooling in hydrogen in the furnace were clean and bright. A lower limit for the contact angle between metal and fused silica just before solidification was estimated as follows. The ingot was mounted on the stage of a co-ordinate comparator fitted with a long-focus eye-piece and orthogonal movements accurate to  $\pm 0.0005$  cm. A straight side of the ingot was aligned with one of the axes of movement to provide a datum axis, the eye-piece being focused on the dia-

lead,  $171^\circ$  for tin, and  $172^\circ$  for indium. The appropriate angles in the capillaries are, of course, always “advancing” contact angles and must be higher still. Thus, unless the contact angle decreases with increase of temperature, which is most unlikely in view of the small negative temperature derivatives of  $-\gamma \cos \theta$  experimentally found, the experimental values of  $-\gamma \cos \theta$  are certainly not more than 2% less than  $\gamma$ ; in fact, it is likely that the error in taking the values of  $-\gamma \cos \theta$  as estimates of  $\gamma$  is less than other experimental errors (see Appendix).

Contact angles of the order of  $140^\circ$  and less were observed by the above technique in experiments where contamination of the melt had occurred.

## III.—DISCUSSION

The present results for the surface tension of lead are somewhat higher than the most reliable previous values. Consistent, reproducible values, higher than previous values, can only be explained as due to the high purity of the material used and the extreme precautions taken

to ensure freedom from contamination. In Fig. 7 the present results are compared with those of Bircumshaw,<sup>7</sup> Matuyama,<sup>8</sup> and Greenaway.<sup>9</sup> The values obtained by Hogness,<sup>10</sup> whose experiments extended only up to 500° C., are virtually coincident with those given by Bircumshaw for this range. Bircumshaw and Greenaway used the maximum-bubble-pressure method, Matuyama the drop-weight method, and Hogness measured the pressure required to force a drop of metal

Those of Matuyama,<sup>8</sup> Pelzel,<sup>11</sup> and Atterton and Hoar<sup>6</sup> are distinctly higher. The liability of the method of Matuyama<sup>8</sup> to give erroneously high results arising from oxide contamination has just been mentioned. Pelzel<sup>11</sup> used a maximum-bubble-pressure method and apparently calculated the results from the simple formula  $-P = 4\gamma/d$ , where  $d$  is the external diameter of the capillary; this relies on  $\theta = 180^\circ$ , since detachment of the bubble is otherwise liable to occur when  $d$  is less than the external

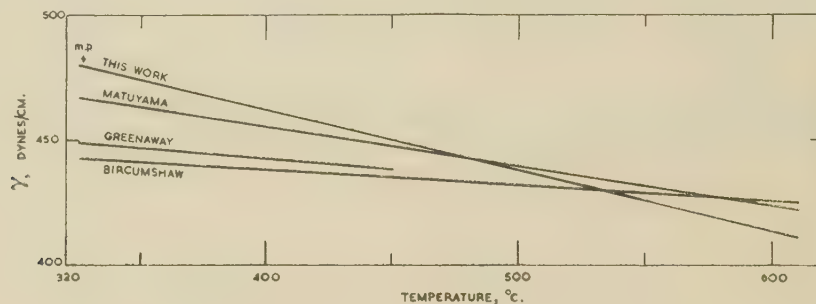


FIG. 7.—Comparison of Results of Various Authors for Lead.

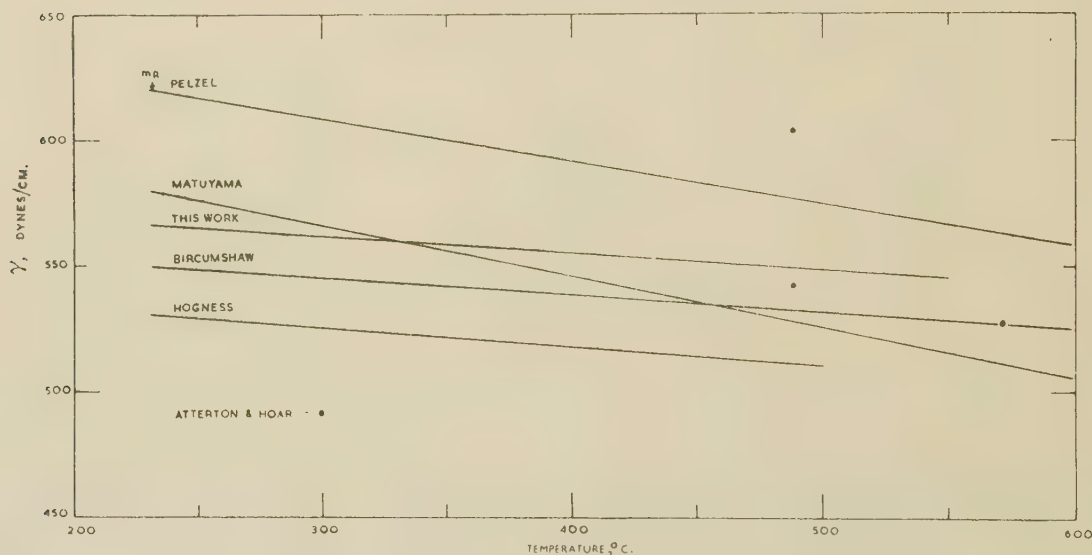


FIG. 8.—Comparison of Results of Various Authors for Tin.

out of the top of a capillary. (The theories involved in these methods are in most cases less exact than the simple capillary theory, and the higher values obtained at lower temperatures in the present work may be partly attributable to this fact, as well as to the greater purity of the metal.) Bircumshaw records difficulty in obtaining concordant results at the lower temperatures. The higher values reported by Matuyama may also be the result of contamination; in the drop-weight method, the cohesive strength of any oxide film formed on the surface of a growing drop delays its breaking free and increases the estimated value of the surface tension.

There is an even wider discrepancy between the results reported for tin by various authors. The present results fall approximately in the centre of the range (Fig. 8).

diameter. The corrections that should be applied in this method have been thoroughly discussed by Taylor;<sup>4</sup> in addition to the need for the true value of  $d$ , gravitational distortion of the bubble from sphericity should be taken into account, and both factors, if ignored, lead to erroneously high values of the surface tension. Smirnova and Ormont,<sup>12</sup> utilizing a modified hanging-drop method, obtained 622 dynes/cm. for  $\gamma_{\text{Sn}_{232}^\circ\text{C.}}$ , which is difficult to assess. Atterton and Hoar<sup>6</sup> obtained  $\gamma_{\text{Sn}_{232}^\circ\text{C.}} = 614$  dynes/cm., but with their ground silica conical capillaries found somewhat variable contact angles in the range  $135^\circ$ – $160^\circ$ ; if these angles were, in fact, erroneously low, the surface tension results were erroneously high. On the whole, we prefer the present determinations to all the above, and to the lower results



of Bircumshaw, which may well have been caused by the less pure tin available to him.

The surface tension of indium is given in "Liquid Metals Handbook"<sup>13</sup> as 340 dynes/cm. in the range 170°–250° C., this being cited as a "preliminary measurement" made at the U.S. Naval Research Laboratory. No other experimental value seems to be available. Estimates made by Taylor,<sup>1</sup> using the empirical relationships between metal surface tension and heat of evaporation<sup>14, 15</sup> and atomic volume,<sup>16, 17</sup> are respectively 630 and 550 dynes/cm. Our value of  $\gamma_{\text{In}_{156}^{\circ}\text{C.}}$  559 dynes/cm. is in very satisfactory harmony with the atomic volume relationship.

Experiments with four lead-tin and four lead-indium alloys, reported in detail elsewhere,<sup>18</sup> gave values for both  $\gamma$  and  $d\gamma/dT$  falling very consistently between those for the pure metals, and in harmony with the thermodynamic theory of mixtures. This is additional evidence for the reliability of the present method.

The molar surface free energy  $G^{\sigma}$ , entropy  $S^{\sigma}$ , enthalpy  $H^{\sigma}$ , and heat capacity  $C_p^{\sigma}$  may be calculated from the

somewhat greater configurational and thermal disorder in the surface layer of the liquid than in the bulk, but the general state of the surface layer is yet far nearer to that of the liquid bulk than it is to that of the vapour.

(2) The molar surface enthalpies are all fairly small fractions of the molar latent heats of evaporation. Only in the case of lead does the ratio  $H^{\sigma}/\lambda^E$  approach 0.25, the value that might be expected<sup>14</sup> in the formation of a close-packed surface layer from a close-packed bulk, since in such a surface a particle has 9 nearest neighbours bonding with it, compared with 12 in the bulk and none in the vapour state. The experimental values <0.25 evidently arise because the simple close-packed model, with a monolayer surface, bonds only between nearest neighbours, and all bonds equivalent, is inadequate. One approach to an improved model is to consider bonds between other than nearest neighbours; while this may be a fruitful method for non-metallic liquids, it seems inappropriate for metals, where it is not easy to visualize, on either the Mott-Jones or the Pauling bonding theories, any substantial bonding between non-nearest neigh-

TABLE I.—Surface Thermodynamic Magnitudes, and Comparison with Absolute Entropy, Latent Heat of Evaporation, and Heat Capacity of Bulk Liquid Metals.

Metal	Temp., °K.	$\gamma$ , dynes. cm. <sup>-1</sup>	$A$ , cm. <sup>2</sup> $\times 10^3$	$d\gamma/dT$ , dynes. cm. <sup>-1</sup> °K. <sup>-1</sup>	$dA/dT$ , cm. <sup>2</sup> °K. <sup>-1</sup>	$G^{\sigma}$ , cal.	$S^{\sigma}$ , cal./°K.	$H^{\sigma}$ , cal.	$C_p^{\sigma}$ , cal./°K.	$S$ , cal./°K.	$\lambda_{B.P.}^E$ , cal.	$C_p$ , cal./°K.
Pb	623	474.4	6.698	−0.24	$5.1 \times 10^4$	7594	3.264	9627	+0.4	22.46	42,700	7.55
	723	450.5	6.749			7267	3.322	9669		23.59		
Sn	623	558.5	6.154	−0.065	$4.0 \times 10^4$	8215	0.422	8478	+0.08	20.82	70,000	7.31
	723	552.0	6.194			8172	0.435	8486		21.91		
In	523	550.0	5.967	−0.10	$4.7 \times 10^4$	7844	0.808	8267	+0.13	19.65	55,500	7.5
	623	540.0	6.014			7762	0.831	8280		20.96		

results, if it is assumed that the surface is one atom thick and the molar surface area  $A$  thus given approximately by

$$A = 1.091 V^{2/3} N^{1/3},$$

where  $V$  is the molar volume and  $N$  the Avogadro number (the expression is exact for a close-packed surface of close-packed spheres). Using values of  $V$  derived from established density measurements,<sup>13</sup> and

$$G_T^{\sigma} = \gamma T A_T,$$

$$S_T^{\sigma} = -\frac{dG^{\sigma}}{dT} = -\gamma T \frac{\partial A}{\partial T} - A_T \frac{\partial \gamma}{\partial T},$$

$$H_T^{\sigma} = G_T^{\sigma} + T S_T^{\sigma},$$

$$C_p^{\sigma} = \frac{dH^{\sigma}}{dT} = T \frac{dS^{\sigma}}{dT},$$

we may calculate the values given in Table I. Values of the molar bulk absolute entropy,  $S$ , the molar latent heat of evaporation at the boiling point,  $\lambda_{B.P.}^E$ , and the molar heat capacity,  $C_p$ ,<sup>19</sup> are given for comparison.

There are several interesting features:

(1) The molar surface entropies are all positive, but very small compared with the molar bulk absolute entropies and with the entropy of evaporation, which is c. 22 for all three metals. Thus in each case there is

bours. A better explanation of values of  $H^{\sigma}/\lambda^E < 0.25$  may be that the bonds remaining on a particle in the surface monolayer have a mean strength greater than that of a bulk bond, as suggested by Oriani;<sup>15</sup> such a concept seems not unreasonable in the light of either of the general theories, since the bonding of any particular metal cation, whether in the bulk or the surface, depends, after all, on its attraction by a plurality of metallic electrons, not by nearest-neighbour cations as such.

(3) The molar surface heat capacities are very small compared with the bulk heat capacities, but all are positive. An increase of surface entropy and enthalpy with increase of temperature means that configurational and thermal disorder, and thermal energy, increase somewhat more rapidly in the surface than in the bulk as temperature rises. This result requires confirmation with very precise data; if it is general, it may be connected with the presence of many more vacancies in the surface monolayer than in the bulk (even in liquids), as discussed by one of us elsewhere.<sup>20</sup> Surface atoms of liquids certainly have greater translational mobility than bulk atoms: if indeed the two possible translational degrees of freedom in the surface contribute more to the heat capacity than the three possible in the bulk, a positive  $C_p^{\sigma}$  would be found. We may note that the gross molar heat capacity of the surface monolayer (the sum of  $C_p$  and  $C_p^{\sigma}$ , since  $C_p^{\sigma}$  is the increase of heat capacity of the

monolayer as compared to the bulk) should be  $8R/2 = 7.90^*$  for 8 fully operative degrees of freedom (6 vibrational, 2 translational), and that the values 7.95, 7.4, and 7.6 for lead, tin, and indium, respectively, approach this value. The molar heat capacity of the bulk liquids would be  $9R/2 = 8.89^*$  for 9 fully operative degrees of freedom (6 vibrational, 3 translational), and the experimental values 7.55, 7.3, and 7.5 must mean that the 3 translational degrees of freedom are only about half operative. At higher temperatures, higher values of  $C_p$ , even approaching 8.89, might be expected, with values of  $C_p^\sigma$  becoming negative and perhaps approaching  $7.90^* - 8.89^* = -0.99$  near the boiling point; no reliable high-temperature data for  $C_p$ , let alone for  $C_p^\sigma$ , seem to be available at present to test this point.

(4) Both the surface and the bulk magnitudes listed in Table I are rather similar for tin and indium, while those for lead are distinctly different. It would clearly be of interest to have reliable data for thallium, to see whether this element, immediately before lead in the atomic series, "pairs" with it as closely as indium does with tin.

#### ACKNOWLEDGEMENTS

Our thanks are due to Mr. A. R. Mathias, of Henry Gardner and Co., Ltd., for kindly supplying the indium used, and to the Department of Scientific and Industrial Research for a Maintenance Allowance to one of us (D. A. M.) during the tenure of which the work was carried out.

#### APPENDIX

##### Elementary Theory

Let  $h_1$  cm. be the reading of the manometer utilizing fluid of density  $\rho_s$  g./cm.<sup>3</sup> when liquid metal of density  $\rho_m$  g./cm.<sup>3</sup> has been forced into a capillary of radius  $r_1$  cm. to a height  $h_m$  below the metal surface outside the capillary (Fig. 9). Then if  $\rho_H$  g./cm.<sup>3</sup> is density of the

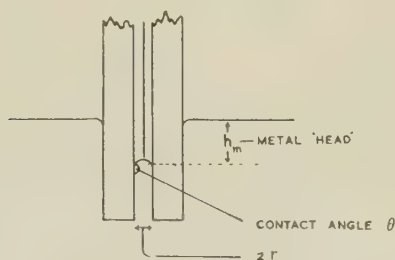


Fig. 9.—Elementary Theory.

gas over the liquid,  $\gamma$  dynes/cm. the surface tension, and  $\theta$  the contact angle

$$g\rho_s h_1 + g(\rho_m - \rho_H)h_m = -\frac{2\pi r_1 \gamma \cos \theta}{\pi r_1^2}.$$

Let  $h_2$  cm. be the corresponding manometer reading for metal at the same height  $h_m$  in a capillary of radius  $r_2$  cm. Then similarly

$$g\rho_s h_2 + g(\rho_m - \rho_H)h_m = -\frac{2\pi r_2 \gamma \cos \theta}{\pi r_2^2},$$

and thus

$$\gamma \cos \theta = -\frac{g\rho_s(h_1 - h_2)}{2(1/r_1 - 1/r_2)}.$$

\* Neglecting the difference between  $C_p$  and  $C_v$ ; the true  $C_p$  values are slightly larger for condensed phases.

##### Meniscus Correction

If the meniscus in a capillary is hemispherical (a near assumption if  $\theta > 171^\circ$ ), it is equivalent to a head of metal

$$\frac{2/3 \pi r^3}{\pi r^2} = \frac{2r}{3}$$

above the circle of contact of metal with the wall of the capillary. The "corrected" height of metal in the capillary is thus  $r/3$  below the top of the meniscus. Thus (Fig. 10), to eliminate the meniscus error for two

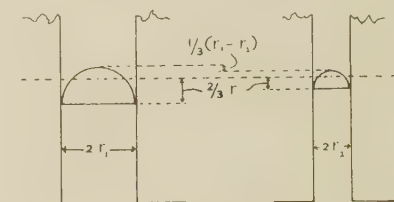


Fig. 10.—Meniscus Correction.

capillaries, the contacting wire in the larger ( $r_1$ ) capillary is raised relative to that in the smaller by an amount  $1/3(r_1 - r_2)$ .

##### Contact Correction

In the larger capillary, the contacting wire cannot easily be centralized, but can be given a point and made to lie against the wall (Fig. 11). Thus, if its

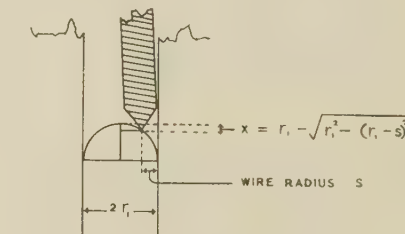


Fig. 11.—Contact Correction.

radius is  $s$  cm., the contact takes place at a height  $r_1 - \sqrt{r_1^2 - (r_1 - s)^2}$  below the top of the meniscus, and the error is eliminated by lowering the contacting wire in the capillary relative to that in the smaller capillary by this amount. No correction is necessary in the smaller capillary if the wire has radius greater than half that of the capillary and is given a square end.

##### Error in Levelling Contact Wires

An accuracy of levelling the ends of the contact wires equivalent to  $\pm 1/20$  of a revolution of the screw adjustment ring was obtainable. The screw being 40 threads to the inch, this corresponds to  $\pm 1/800$  in. =  $\pm 0.0032$  cm., and leads to an error in  $\gamma$  of  $\pm 0.1\%$ .

##### Errors in Capillary Radii

Capillary bore diameters were measured with a microscope having a micrometer gauge, fitted in the focal



plane of the eye-piece, reading to 0.0001 cm. This instrument was checked with a graticule and found to be accurate to  $\pm 0.0001$  cm. Thus the radius error is  $\pm 0.00005$  cm., amounting in the smaller capillary to  $\pm 0.25\%$ . The error in the final value of  $\gamma$  due to this cause is  $\pm 0.4\%$ .

#### Errors in Manometer

The density  $\rho_s$  of the silicone used in the manometer was determined to  $\pm 0.1\%$  as 1.0750 g./cm.<sup>3</sup> at 17° C. and 1.0766 g./cm.<sup>3</sup> at 15° C. Thus the total error in  $\rho_s$  at the ambient temperature of  $17^\circ \pm 2^\circ$  C. was  $\pm 0.25\%$ , leading to the same error in  $\gamma$ .

The manometer could be read to  $\pm 0.05$  cm., leading to an error of *c.*  $\pm 0.25\%$  in  $\gamma$ . The error caused by drainage in the manometer tubes, and the error (in the opposite sense) caused by incorrect timing in the isolation of the manometer from the system, were made negligible by the use of a consistent routine of working and reading of the instrument, so that the small, equal, and opposite errors in  $h_1$  and  $h_2$  disappeared in  $(h_1 - h_2)$ .

The total error in  $\gamma$  due to the manometer may thus be put at  $\pm 0.5\%$ .

#### Overall Error

The total error in  $\gamma$  due to capillary measurement, contact wire height, and the manometer may thus be estimated as  $\pm(0.1 + 0.4 + 0.5) = \pm 1.0\%$ . The error in  $T$  as measured by thermocouple may be estimated as

$\pm 3^\circ$  C. These estimates are extreme limits, but on the other hand do not include fluctuations due to fallibility of observation; they are probably not far from the statistical standard errors.

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# 1743 STRAIN FIGURES APPEARING ON THE SURFACE OF COPPER ELECTRODEPOSITS SUBJECTED TO FATIGUE\*

By M. SUZUKI†

## SYNOPSIS

The effects of the microstructure of the underlying metal upon the flecks and strain figures appearing on the surface of electroplated copper subjected to fatigue have been investigated.

Flecks do not occur at random positions, but appear in the region of the grain boundaries of the metal beneath. Moreover, the grain boundaries on which the flecks appear run parallel to the directions of the planes of the maximum shear stress. The maximum shear strain at the surface of the electrodeposited copper coatings below which no flecks occur has a certain limiting value under constant conditions of testing.

## I.—INTRODUCTION

COPPER coatings electroplated on carbon-steel specimens have been found by Okubo<sup>1</sup> to exhibit "flecking" when the test specimens are subjected to fatigue. The value of the critical stress below which no flecks appear depends on the conditions of experiment. Below this stress the copper coating is unaffected, and above it the depth of colour and density of the flecks increase with increasing load so long as the underlying material of the test specimens remains within the elastic range. By this method the stress-concentration factors in shafts with transverse holes have been determined<sup>2</sup> on the assumption that the magnitude of the critical stress has a constant value under given experimental conditions, though much has still to be learnt about the mechanism of the formation of the flecks. Thus the magnitude of stress at the surface of any shaped part can be determined. On the other hand, the conventional methods of stress measurement, using brittle coatings or sensitive strain gauges, are not applicable to such a problem because the maximum stress occurs in the bores and not at the outer surface. Moreover, considerable difficulty is encountered because of the non-symmetrical nature of the specimen.

Applying the electroplating method to brasses stressed in repeated torsion and rotating bending, the present author<sup>3</sup> has observed that the flecks occur mainly parallel to the directions of the planes of maximum shear stress. Consequently, the distribution of stress, which is as important as the magnitude of the stress, can be estimated by observing the orientations of the flecks.

In the present work, concerned mainly with copper alloys as the underlying material, the strain figures due to flecking, the disposition of the flecks, and the magnitude of the critical maximum shear strain have been studied.

## II.—EXPERIMENTAL

### 1. STRAIN FIGURES

As is well known, Lüders lines or strain figures appear on the polished surfaces of mild steel at the yield point, and a remarkably regular orientation of these layers of slip occurs with respect to the directions of the principal

stresses. Again, on bars of mild steel covered with a coating of rust or mill scale, strain figures may be observed if the bars have been loaded beyond the yield point. By observing the initial cracks and their subsequent spreading as the load is increased, the nature and approximate magnitude of the stress may be estimated. These strain figures, however, can be used only as an indication of yielding in mild-steel specimens, because strain of the order of 1% or more is necessary to provide

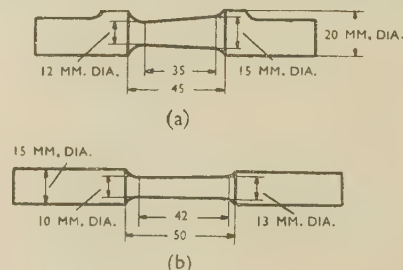


FIG. 1.—Shape and Dimensions of Specimens: (a) for repeated torsion tests, and (b) for rotating-bending tests.

visible evidence. On the other hand, upon the application of load to a test specimen coated with a lacquer which becomes brittle on drying, the coating will obviously crack first at the point where the tensile stress is greatest, and the direction of this first crack will be normal to the direction of the tensile stress. On subsequently increasing the load, the cracks spread and the stress-coat pattern is observed. However, this method requires a high degree of skill to obtain a coating of uniform thickness if the shape of the specimen is irregular, for the uniformity of the coating affects the results considerably. Furthermore, in the results obtained by means of strain-indicating brittle coatings, there is a possibility of error occurring owing to Poisson's ratio being different from that of common metals, and owing to appreciable creep under sustained load. By the electroplating method, however, the magnitude and distribution of stress in metals can be determined in the low-stress range by observation of the strain figures

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appearing on the surface of copper coatings electroplated on to them.

In order to investigate the effects of the microstructure of the basis metal upon the strain figures, ( $\alpha + \beta$ ) and  $\alpha$  cold-rolled brasses and sand-cast bronzes were studied. The shapes and dimensions of the test specimens are illustrated in Fig. 1. The surfaces of the specimens were abraded on a series of fine emery papers, rinsed successively in trichlorethylene, acetone, and alcohol, and then given a preliminary strike in copper cyanide solution. The conditions for plating, similar to those employed by Okubo,<sup>1</sup> were as follows:

Solution: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	250 g.
$\text{H}_2\text{SO}_4$ (sp. gr. 1.84)	80 g.
$\text{H}_2\text{O}$	1000 c.c.
Current density	3 amp./dm. <sup>2</sup>
Temperature of plating	15° C.
Time of plating	15 min.

Zinc sulphate, employed by Okubo as an addition, was not used in this investigation. After the copper had been deposited, the specimens were subjected to repeated-torsion and rotating-bending tests. The testing machines employed were run at 1800 r.p.m. for both methods of testing.

The strain figures obtained after  $5 \times 10^6$  cycles of stress of suitable magnitude are illustrated. Figs. 2 (a) and (b) (Plate XXXVIII) show the strain figures obtained in repeated-torsion and rotating-bending tests, respectively, when ( $\alpha + \beta$ ) brasses were employed as the basis material. The twisting and bending moments were  $\pm 1.75$  and  $\pm 1.17$  kg.m., respectively. From Fig. 2 (a) it can be seen that the flecks run parallel to the axial direction of the test specimen, and from Fig. 2 (b) that the orientation of the flecks lies at an angle of 45° with respect to the axis of the specimen. These orientations of the flecks can in both cases be seen more distinctly in the photomicrographs shown in Fig. 3 (Plate XXXVIII). Fig. 3 (a) illustrates the flecks under torsion testing and Fig. 3 (b) shows them under bend testing. From these photographs it may be observed that the disposition of the flecks occurs parallel to the directions of the planes of the maximum shear stress, and that the density of the flecks depends on the magnitude of the stress.

When  $\alpha$ -brasses were used as specimens, the strain figures obtained under torsion and rotating-bending tests were as shown in Figs. 5 (a) and (b) (Plate XXXVIII). The twisting and bending moments were  $\pm 1.56$  and 1.02 kg.m., respectively. Photomicrographs of the flecks are shown in Figs. 6 (a) and (b) (Plate XXXVIII). In these cases also the flecks run in the directions of the planes of maximum shear stress, though the size and shape of the flecks are markedly different from those for specimens of ( $\alpha + \beta$ ) brass. On comparing the photomicrographs of the flecks with those of crystal grains of the basis material, illustrated in Fig. 4 (Plate XXXVIII) for ( $\alpha + \beta$ ) brass and in Fig. 7 (Plate XXXVIII) for  $\alpha$ -brass, it is clear that the flecks are the same order of magnitude as the crystal grains of the underlying metal in each case.

Figs. 8 (a) and (b) (Plate XXXIX) show the strain figures when specimens of sand-cast bronzes containing 6% tin were subjected to torsion and rotating-bending tests, respectively. The twisting and bending moments were

$\pm 1.18$  and  $\pm 0.82$  kg.m., respectively. It is observed that the border lines of the markings are parallel to the directions of the planes of the maximum shear stress, but that the dimensions of the markings are large compared with those of rolled brass specimens. Under the microscope it could be seen that a fleck consisted of a cluster of minute flecks disposed along the directions of the planes of maximum shear stress, as illustrated in Fig. 9 (Plate XXXIX), showing the flecks due to torsion (a) and the flecks due to rotating bending (b). On comparing the photomicrograph with that of the crystal grains of sand-cast bronze shown in Fig. 10 (Plate XXXIX), it seems that the size of the fleck is approximately equal to that of the grains.

From the results of the experiment described, it has been established that the flecks appearing on the surfaces of electrodeposited copper lie in the directions of the planes of the maximum shear stress and that their size and shape are similar to those of the crystal grains of the underlying metal.

## 2. EFFECT OF THE MICROSTRUCTURE OF THE UNDERLYING METAL UPON THE STRAIN FIGURES

From what has already been said, it is clear that the flecks appearing on the surfaces of electrodeposited copper subjected to fatigue are affected by the microstructure of the material beneath. In order to ascertain the relationship between the flecks and the crystal grains of the basis metals, the position of the flecks in relation to that of the grains was studied. A copper-coated specimen was polished electrolytically after flecks had appeared and was observed under the microscope at a fixed point on the test specimen. The example of flecks shown in Fig. 11 (a) (Plate XL) relates to an  $\alpha$ -brass test specimen subjected to a rotating-bending test. The conditions for electropolishing were as follows:

Solution: $\text{H}_3\text{PO}_4$ (sp. gr. 1.70)	250 g.
$\text{H}_2\text{O}$	1000 c.c.
Current density	5 amp./dm. <sup>2</sup>

During electropolishing the deposited copper, except in the region of the flecks, was first removed anodically, and the grain boundaries of the basis metal appeared in some places, as shown in Fig. 11 (b) (Plate XL). The further polishing proceeded, the more copper was removed, and the grain boundaries appeared more clearly as shown in Fig. 11 (c) (Plate XL). From Fig. 11 (a) and (c), the positions of the flecks relative to the crystal grains of the basis metal are reproduced schematically in Fig. 12 (Plate XL). In this figure the grain boundaries are represented by full lines, and the positions originally occupied by the flecks are shown by dotted areas. From this figure it will be noted that flecks do not occur at random, but mainly in the region of the grain boundaries of the underlying metal. The flecks form first at the grain boundaries of the basis metal that lie parallel to the directions of the planes of the maximum shear stress, and grow with increasing load and number of repetitions of the stress.

In electrodeposits, the layer first deposited generally has a microstructure similar to that of the underlying metal, provided that the surface is clean; the crystal structure is of the same type and the lattice parameters are not widely different.<sup>4</sup> The thickness of the copper

deposits used in this investigation was about 0.01 mm., and the preferred orientation which is seen in thick deposits was therefore not observed. Hence, it may be assumed that the behaviour of the deposited copper when stressed is similar to that of the basis metal.

Since the flecks are influenced by the microstructure of the basis metal, as described above, the effects of the microstructure upon the strain figures must be considered. For example, the flecks would be expected to lie along the directions parallel and perpendicular to the axis of the test specimens in the torsion tests of circular shafts, because the flecks occur preferentially in the orientations parallel to the directions of the planes of maximum shear stress. However, in the cases of the test specimens taken from rolled brass bars, the strain figures consist only of flecks parallel to the axial direction, as shown in Figs. 2 (a) and 5 (a). This may be explained by the fact that the orientation of the grain boundaries is predominantly in the axial direction, because the rolled bars have a fibrous structure parallel to the direction of rolling.

In the case of carbon-steel specimens, however, the flecks apparently do not lie parallel to the directions of the planes of maximum shear stress, as shown in Fig. 13 (Plate XL). Careful observation under the microscope reveals, however, that each fleck indicates the direction of maximum shear stress (Fig. 14, Plate XL). This is because the crystal grains of carbon steel are small compared with those of rolled brasses. Hence, in order to estimate the distribution of stresses from the strain figures, it is necessary to know the microstructure of the underlying material.

### 3. VALUE OF THE CRITICAL SHEAR STRAIN

It is not difficult to assume that the formation of the flecks appearing on the surface of copper electroplated coatings is attributable to the relative shear movement of neighbouring crystals. This can be confirmed from Fig. 12. Consequently, one of the most important factors influencing the formation of flecks is probably the maximum shear stress in the basis metal. In order to determine the magnitude of the critical stress under certain experimental conditions in this investigation, 0.9% carbon steel and ( $\alpha + \beta$ ) and  $\alpha$  brasses were employed as basis materials. The shapes and dimensions of the specimens were the same as those illustrated in Fig. 1. The conditions for plating were also as previously described. Many factors, such as the solution composition, current density, degree of agitation, temperature, and geometry of the substrate, influence the crystal structure of electrodeposits. These factors have been kept as constant as possible in determining the magnitude of the critical stress. Repeated-torsion and rotating-bending

tests were carried out as before. The limiting positions of the flecks that appeared, after  $5 \times 10^6$  cycles of repeated stressing, were measured by means of a reading microscope, and the maximum shear stress in torsion and the normal stress in rotating bending at the surface of the test specimens were calculated. In rotating-bending tests, the relation :

$$\tau' = \frac{1}{2}\sigma$$

holds, where  $\tau'$  is the maximum shear stress and  $\sigma$  the normal stress. The critical stresses  $\sigma_c$  and  $\tau_c$  obtained by rotating-bending and repeated-torsion tests, respectively, and the calculated maximum shear strain  $\gamma_c$  in each case are shown in Table I. The moduli of elasticity

TABLE I.—*The Value of the Critical Shear Strain.*

Basis Material	$G$ , kg./mm. <sup>2</sup>	Rotating Bending			Torsion	
		$\sigma_c$ , kg./mm. <sup>2</sup>	$\tau'_c = \sigma_c/2$ , kg./mm. <sup>2</sup>	$\gamma_c$ , %	$\tau_c$ , kg./mm. <sup>2</sup>	$\gamma_c$ , %
0.9% carbon steel	$0.778 \times 10^4$	$\pm 15.5$	$\pm 7.75$	$\pm 0.100$	$\pm 7.93$	$\pm 0.102$
( $\alpha + \beta$ )-brass.	$0.355 \times 10^4$	$\pm 7.24$	$\pm 3.62$	$\pm 0.102$	$\pm 3.59$	$\pm 0.101$
$\alpha$ -brass.	$0.290 \times 10^4$	$\pm 5.75$	$\pm 2.87$	$\pm 0.099$	$\pm 2.85$	$\pm 0.098$

in shear ( $G$ ) used in calculating the strains have been measured on a test-piece having a diameter of 2.5 mm. taken from the same bars as the test specimens. It should be noted from the results in Table I that the critical maximum shear stresses vary with the basis material, whereas the magnitude of the critical maximum shear strains is constant irrespective of the basis material. Accordingly, it may be stated that the flecks appear at the positions where the repeated maximum shearing strain reaches the value of  $\pm 0.10\%$  under the conditions of this investigation, and that the orientations of the flecks are parallel to the directions of maximum shear strain.

### ACKNOWLEDGEMENTS

The author wishes to express his thanks to Professor Emeritus S. Higuchi, Tohoku University, and Professor H. Okubo, Nagoya University, for their interest and encouragement, and to Mr. T. Murayama for assistance in obtaining the experimental data.

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2. H. Okubo and S. Sato, *J. Appl. Mechanics*, 1955, **22**, 193.
3. M. Suzuki, *Bull. Inst. Metals*, 1955, **2**, (19), 227.
4. A. G. Gray *et al.*, "Modern Electroplating", p. 27. 1953: New York (John Wiley and Sons, Inc.); London (Chapman and Hall, Ltd.).



MICROSECTIONS OF 0.050-IN. AL-ZN-MG ALLOY SHEET HEAT-TREATED AT 460° C.  $\times 100$ .

High-Purity Alloys

Commercial-Purity Alloys

6  
WZ111  
WZ67  
WZ312  
WZ88  
WZ413  
WZ99  
WZ514  
WZ1010  
XWC15  
XWF

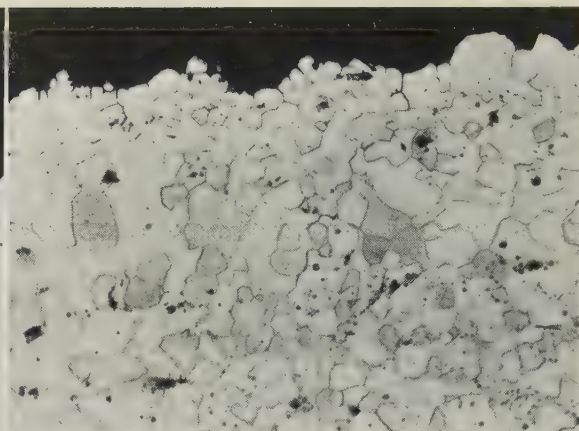
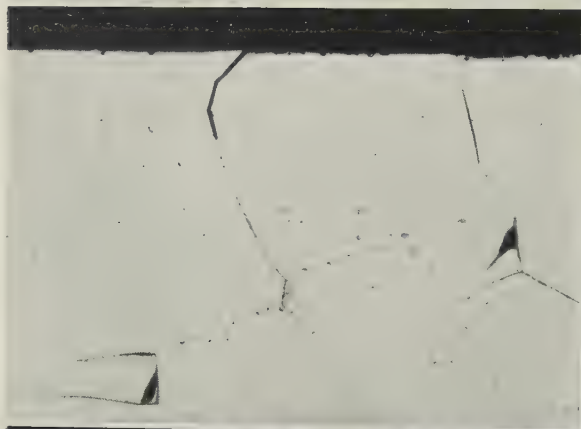
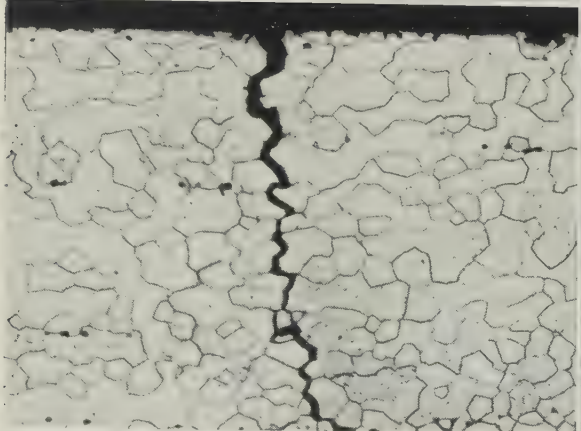
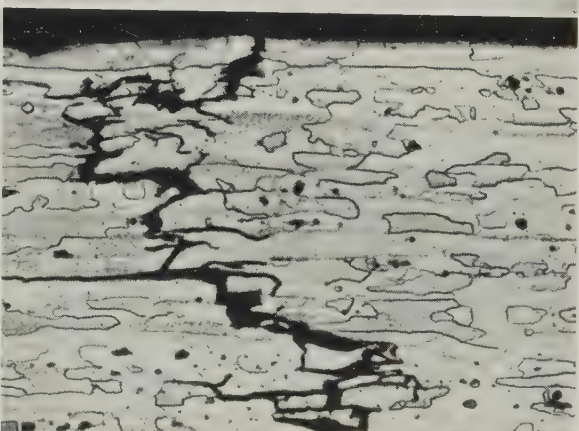
FIGS. 6 and 11.—Ternary Al-Zn-Mg Alloy.

FIGS. 7 and 12.—1.25% Cu Addition.

FIGS. 8 and 13.—0.25% Mn Addition.

FIGS. 9 and 14.—0.25% Cr Addition.

FIGS. 10 and 15.—1.25% Cu + 0.25% Mn + 0.25% Cr Addition.

16  
WZ317  
WZ418  
WZ119  
WZ320  
XWE21  
XWF

FIGS. 16 and 17.—Stress-Corrosion Fractures of High-Purity Alloys Aged at Room Temperature.  $\times 100$ .

FIG. 16.—1.25% Cu (WZ3).

FIG. 17.—0.25% Mn (WZ4).

FIGS. 18 and 19.—Corrosion in Salt-Peroxide Solution of High-Purity Alloys Aged at Room Temperature.  $\times 100$ .

FIG. 18.—Ternary Al-Zn-Mg Alloy (WZ1).

FIG. 19.—1.25% Cu (WZ3).

FIGS. 20 and 21.—Stress-Corrosion Cracking in Bent Specimens of Fully Heat-Treated Commercial-Purity Alloys.  $\times 250$ .

FIG. 20.—1.25% Cu + 0.25% Mn (XWE).

FIG. 21.—1.25% Cu + 0.25% Mn + 0.25% Cr (XWF).



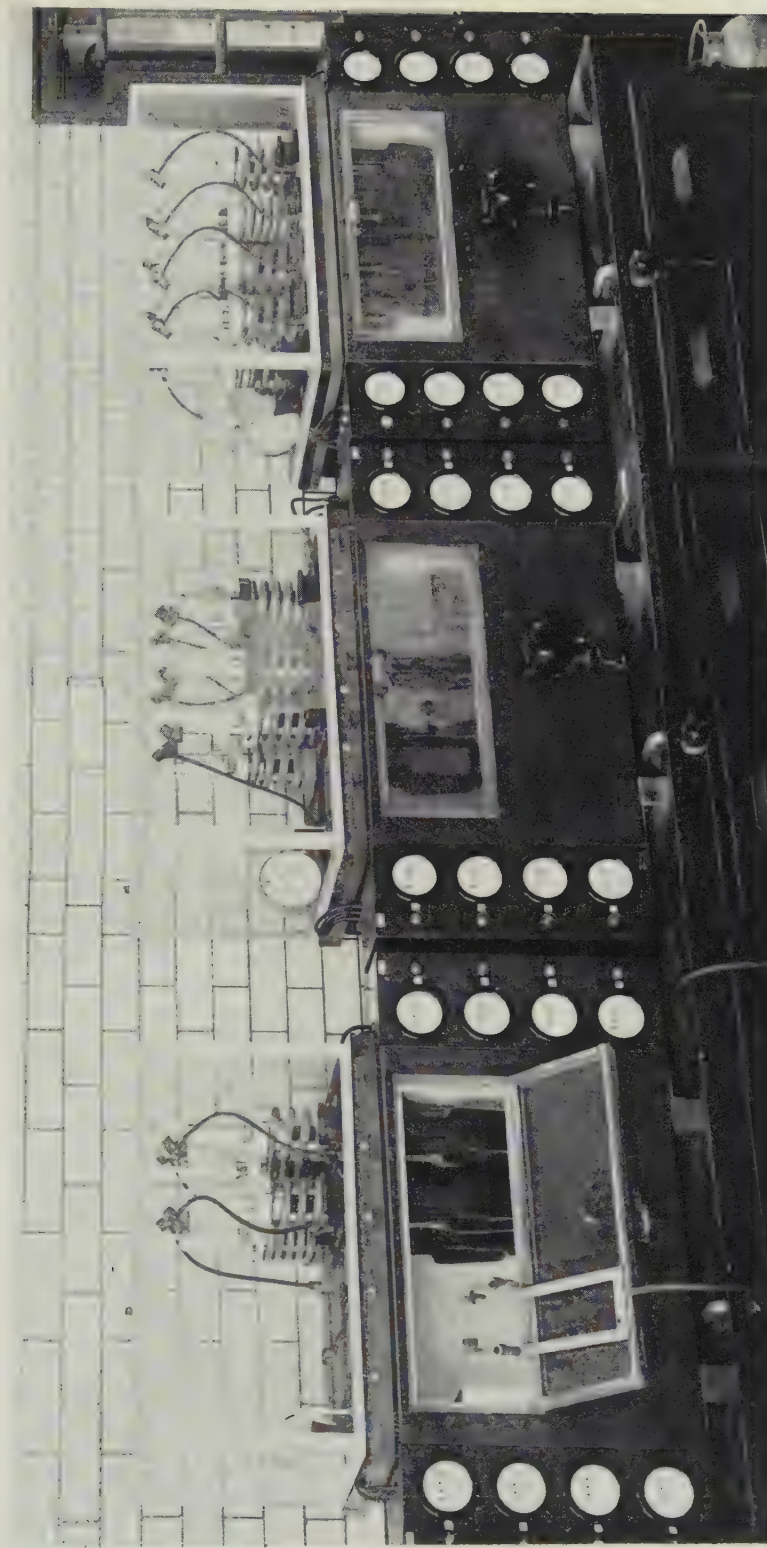


FIG. 22.—Cabinets with Stress Units and Control Gear.

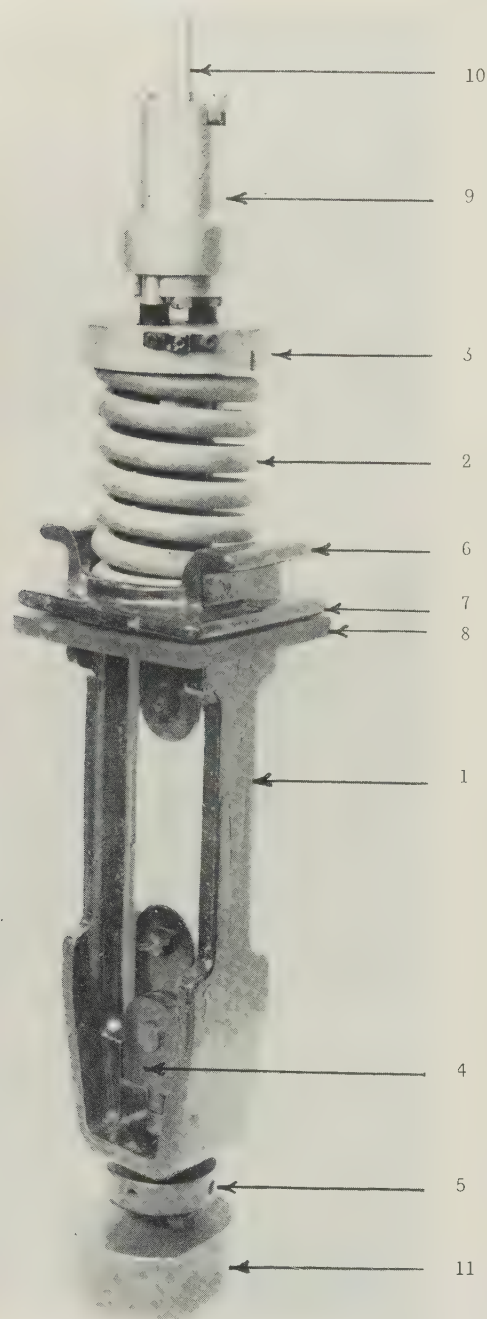


FIG. 23.—Stress Unit Fitted with Loading Adaptor Nut. (For description see Appendix, p. 169.) Approx.  $\frac{1}{4}$  size.

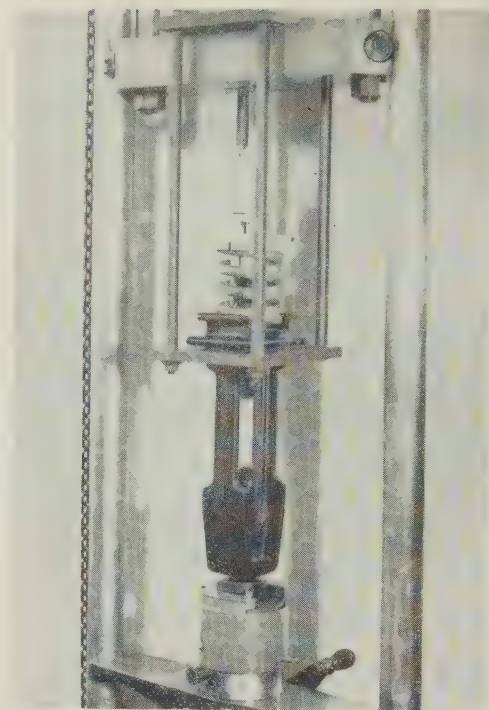


FIG. 24.—Stress Unit in Loading Position in Tensile Machine.

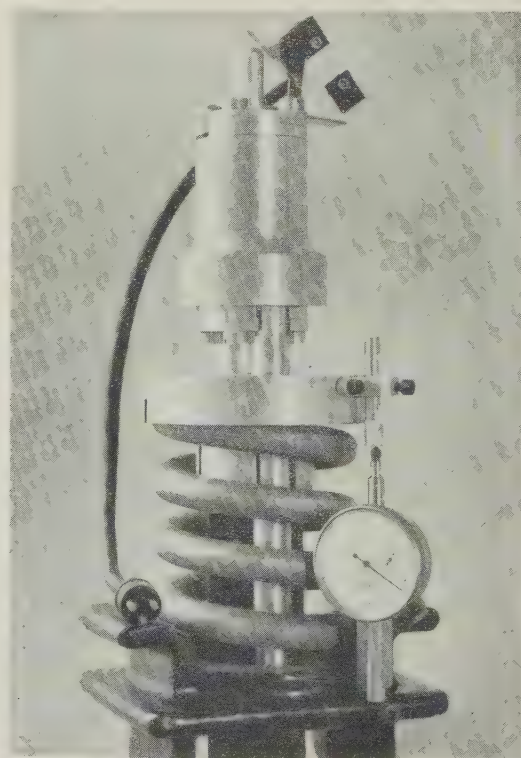


FIG. 25.—Stress-Unit Head with Microswitch and Dial Gauge.





FIGS. 1-2.—As-Polished Surfaces of Copper. Phase-contrast illumination. 250.

FIG. 1.—Polished on (0-1)  $\mu$ -grade diamond.

FIG. 2.—Polished on (0-0.1)  $\mu$ -grade alumina.

FIGS. 3-8.—Polished Surfaces of Copper Covered with Thin Deposit of Copper.

FIG. 3.—Polished on (0-1)  $\mu$ -grade diamond; bright-field illumination.  $\times 250$ .

FIG. 4.—Same field as Fig. 3; polarized light.  $\times 250$ .

FIG. 5.—Polished on (0-0.1)  $\mu$ -grade alumina; bright-field illumination.  $\times 250$ .

FIG. 6.—Same field as Fig. 5; polarized light.  $\times 250$ .

FIG. 7.—Polished on magnesium oxide by normal method.  $\times 2000$ .

FIG. 8.—Polished on magnesium oxide by skidding method.  $\times 2000$ .



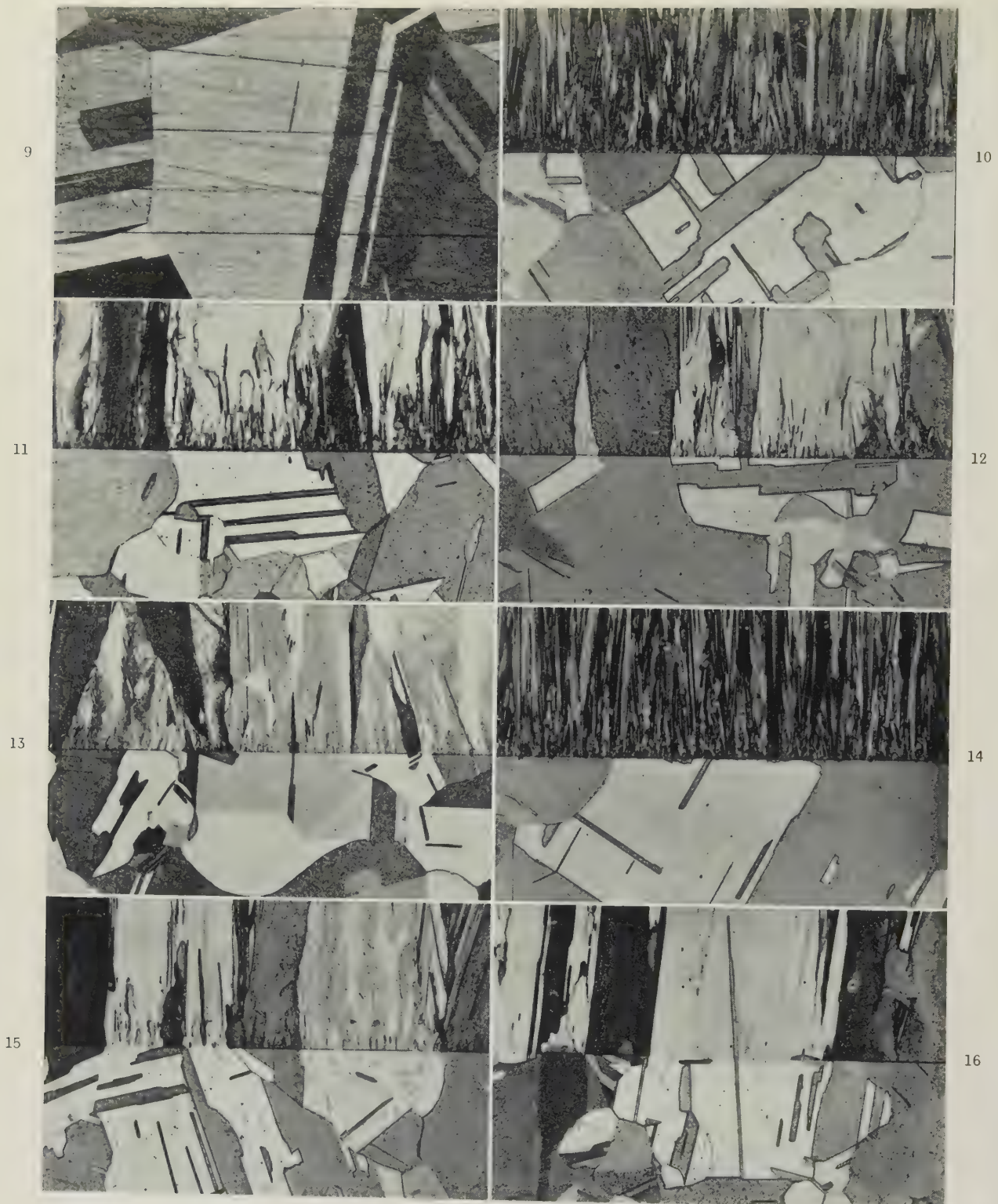


FIG. 9.—Polished Surface of 70 : 30 Brass Covered with Thin Deposit of Copper. Polished on (0-1)  $\mu$ -grade diamond and then by skidding on magnesium oxide for 10 min.  $\times 250$ .

FIGS. 10-16.—Sections of Deposits of Copper on Polished Surfaces of Copper. Etched in ferric chloride reagent.  $\times 250$ .

FIG. 10.—Polished on (0-1)  $\mu$ -grade diamond.

FIG. 11.—Polished on (0-2)  $\mu$ -grade alumina.

FIG. 12.—Polished on (0-0-1)  $\mu$ -grade alumina.

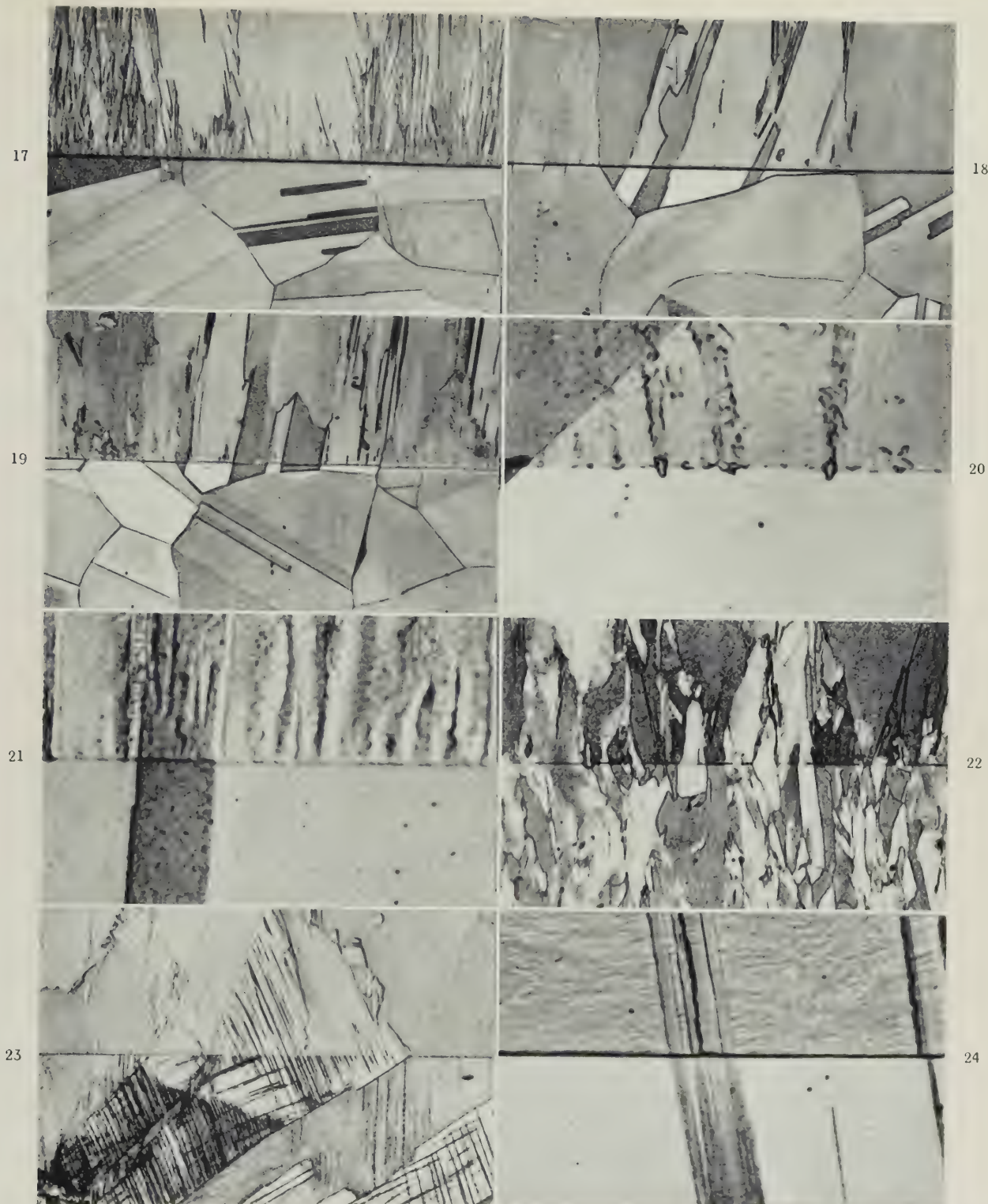
FIG. 13.—Polished on magnesium oxide by normal method.

FIG. 14.—Polished on (0-0-1)  $\mu$ -grade alumina but containing gross deformation remaining from abrasion.

FIG. 15.—Polished on (0-1)  $\mu$ -grade diamond and then by skidding on magnesium oxide for 10 min.

FIG. 16.—Polished on (0-1)  $\mu$ -grade diamond and then by skidding on magnesium oxide for 20 min.





FIGS. 17-20.—Sections of Deposits of Copper on Polished Surfaces of 70 : 30 Brass. Etched in ferric chloride reagent.

FIG. 17.—Polished on (0-0.1)  $\mu$ -grade alumina.  $\times 250$ .

FIG. 18.—Polished on magnesium oxide by normal method.  $\times 250$ .

FIG. 19.—Polished on (0-1)  $\mu$ -grade diamond and then by skidding on magnesium oxide for 5 min.  $\times 250$ .

FIG. 20.—As for Fig. 19, but taper-sectioned at nominal taper ratio of 10.  $\times 2000$ . This micrograph is explained by the sketch in Fig. 33 (p. 180 of text).

FIG. 21.—Section of Deposit of Copper on Copper. Surface polished on (0-1)  $\mu$ -grade diamond and then by skidding on magnesium oxide for 5 min. Ferric chloride etch. Oblique illumination.  $\times 2000$ .

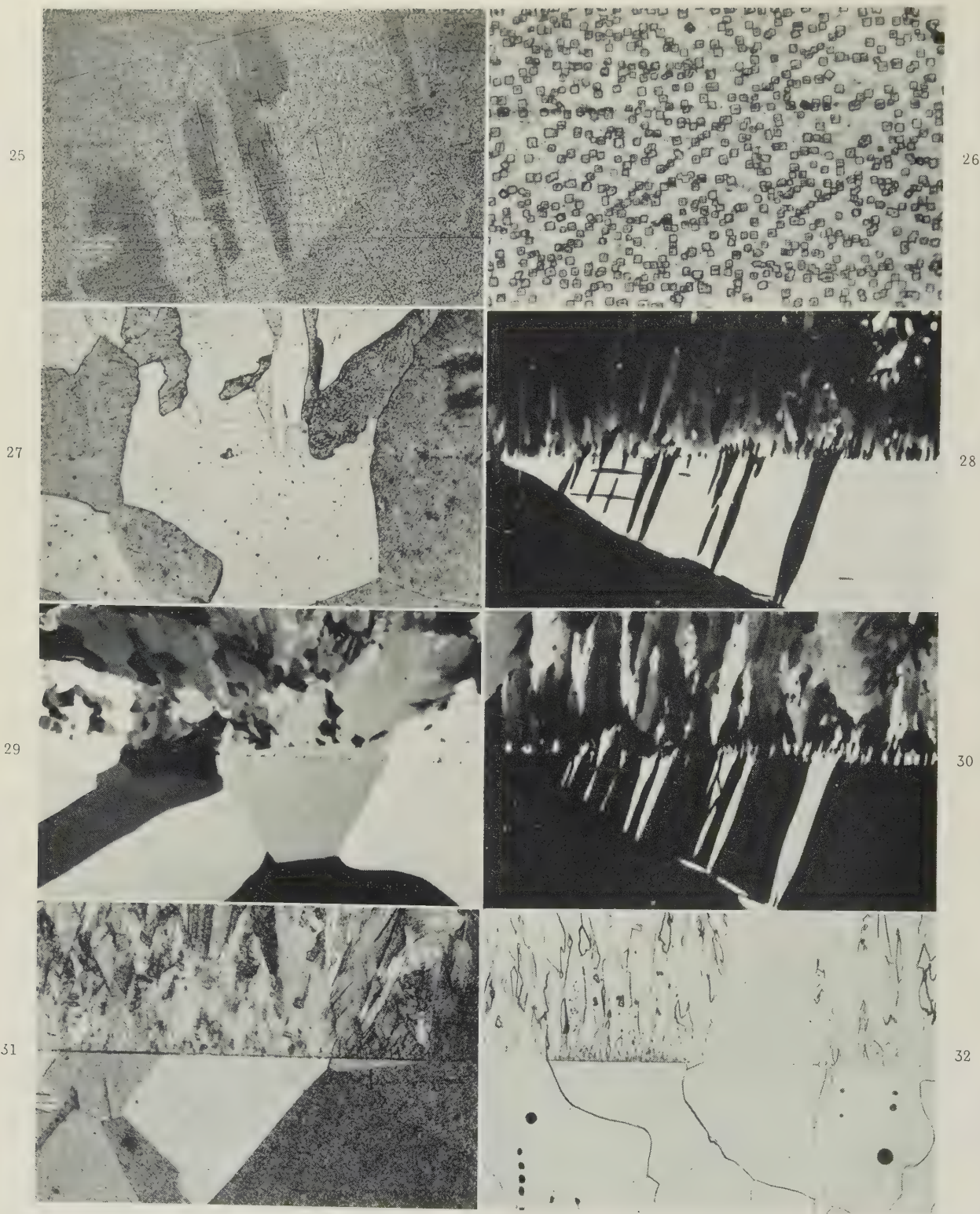
FIGS. 22-24.—Section of Deposits on Copper and Brass Specimens Subjected to Prior Deformation. Ferric chloride etch.

FIG. 22.—Copper, compressed 60%.  $\times 250$ .

FIG. 23.—70 : 30 Brass, compressed 20%. Oblique illumination.  $\times 250$ .

FIG. 24.—90 : 10 Brass, compressed 20%. Oblique illumination.  $\times 2000$ .





FIGS. 25-26.—Overgrowths of Alkali Halides on Surface of Silver Polished on (0-0.1)  $\mu$ -grade Alumina.

FIG. 25.— $\times 50$ .

FIG. 26.— $\times 500$ .

FIG. 27.—Section of Deposit of Tin on Tin Surface Polished on (0-1)  $\mu$ -grade Diamond. Etched in ammonium persulphate reagent.  $\times 100$ .

FIGS. 28-30.—Sections of Deposits of Zinc on Zinc Surfaces. Polarized light.  $\times 250$ .

FIG. 28.—Polished on (0-1)  $\mu$ -grade diamond.

FIG. 29.—Polished on (0-0.1)  $\mu$ -grade alumina.

FIG. 30.—Same field as Fig. 28, rotated through  $90^\circ$ .

FIG. 31.—Section of Deposit of Silver on Silver Surface Polished on (0-0.1)  $\mu$ -grade Alumina. Etched in potassium dichromate reagent.  $\times 250$ .

FIG. 32.—Section of Deposit of Iron on Iron Surface Polished on (0-0.1)  $\mu$ -grade Alumina. Etched in nital reagent.  $\times 250$ .



## PHOTOMICROGRAPHS OF TITANIUM-ALUMINIUM-OXYGEN ALLOYS

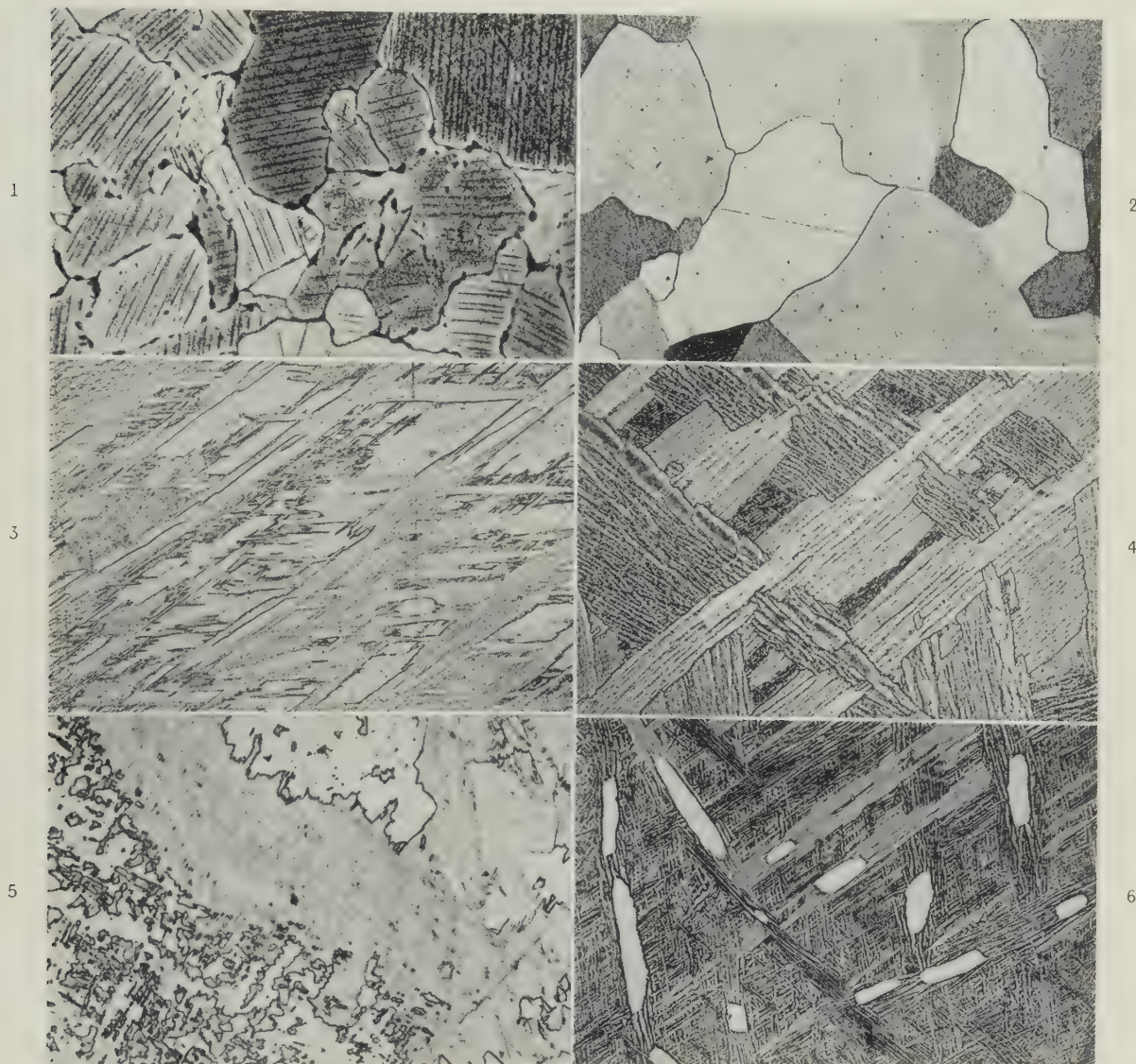


FIG. 1.—5% Al, 0.05% O<sub>2</sub>. 4 hr. at 1100° C., water-quenched; 24 hr. at 925° C., water-quenched. Duplex structure.  $\times 75$ .

FIG. 2.—5% Al, 0.05% O<sub>2</sub>. 4 hr. at 1100° C., water-quenched; 4 hr. at 900° C., in vacuum, furnace-cooled; 24 hr. at 925° C., water-quenched. Single-phase structure.  $\times 75$ .

FIG. 3.—1% Al, 0.5% O<sub>2</sub>. 4 hr. at 1100° C., water-quenched; 4 hr. at 850° C. in vacuum, furnace-cooled;  $\frac{1}{2}$  hr. at 1050° C.,  $\frac{1}{2}$  hr. at 1020° C., drastically quenched. Fine "transformed  $\beta$ " structure.  $\times 75$ .

FIG. 4.—As Fig. 3, but 5 seconds' delay before quenching. Coarse "transformed  $\beta$ " structure.  $\times 75$ .

FIG. 5.—5% Al, 0.05% O<sub>2</sub>. 4 hr. at 1100° C., water-quenched; 4 hr. at 900° C. in vacuum, furnace-cooled; 18 hr. at 1025° C., water-quenched.  $\beta$ .  $\times 150$ .

FIG. 6.—2.5% Al, 1% O<sub>2</sub>. 1 hr. at 1300° C., water-quenched; 4 hr. at 900° C. in vacuum, furnace-cooled; 4 hr. at 1150° C., water-quenched.  $\alpha + \beta$ .  $\times 75$ .



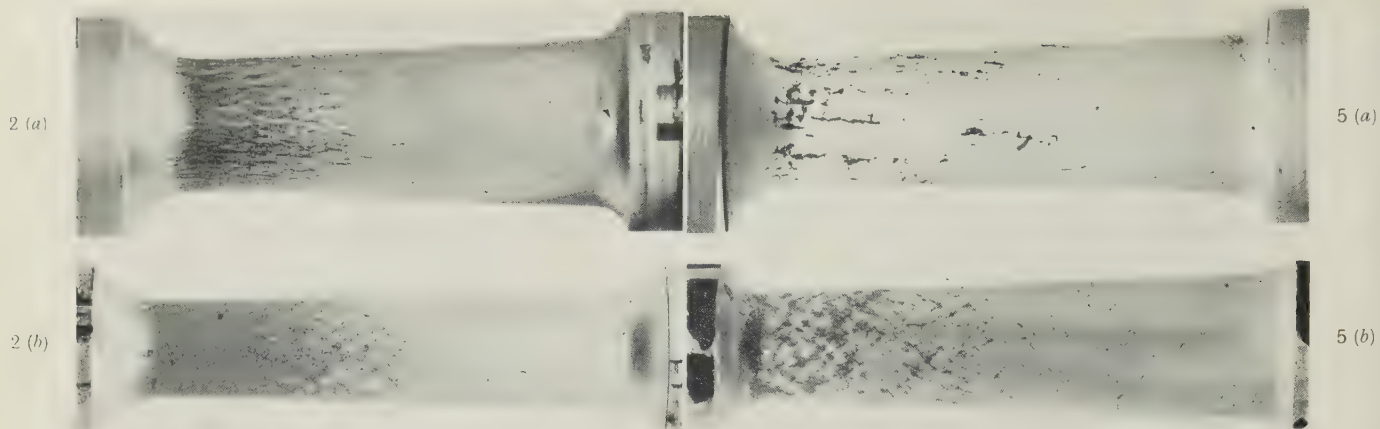


FIG. 2.—Strain Figure Appearing on the Surface of Electroplated Copper on an  $(\alpha + \beta)$  Brass Test Specimen: (a) Torsion Test; (b) Rotating-Bending Test.

FIG. 5.—Strain Figure Appearing on the Surface of Electroplated Copper on an  $\alpha$ -Brass Test Specimen: (a) Torsion Test; (b) Rotating-Bending Test.

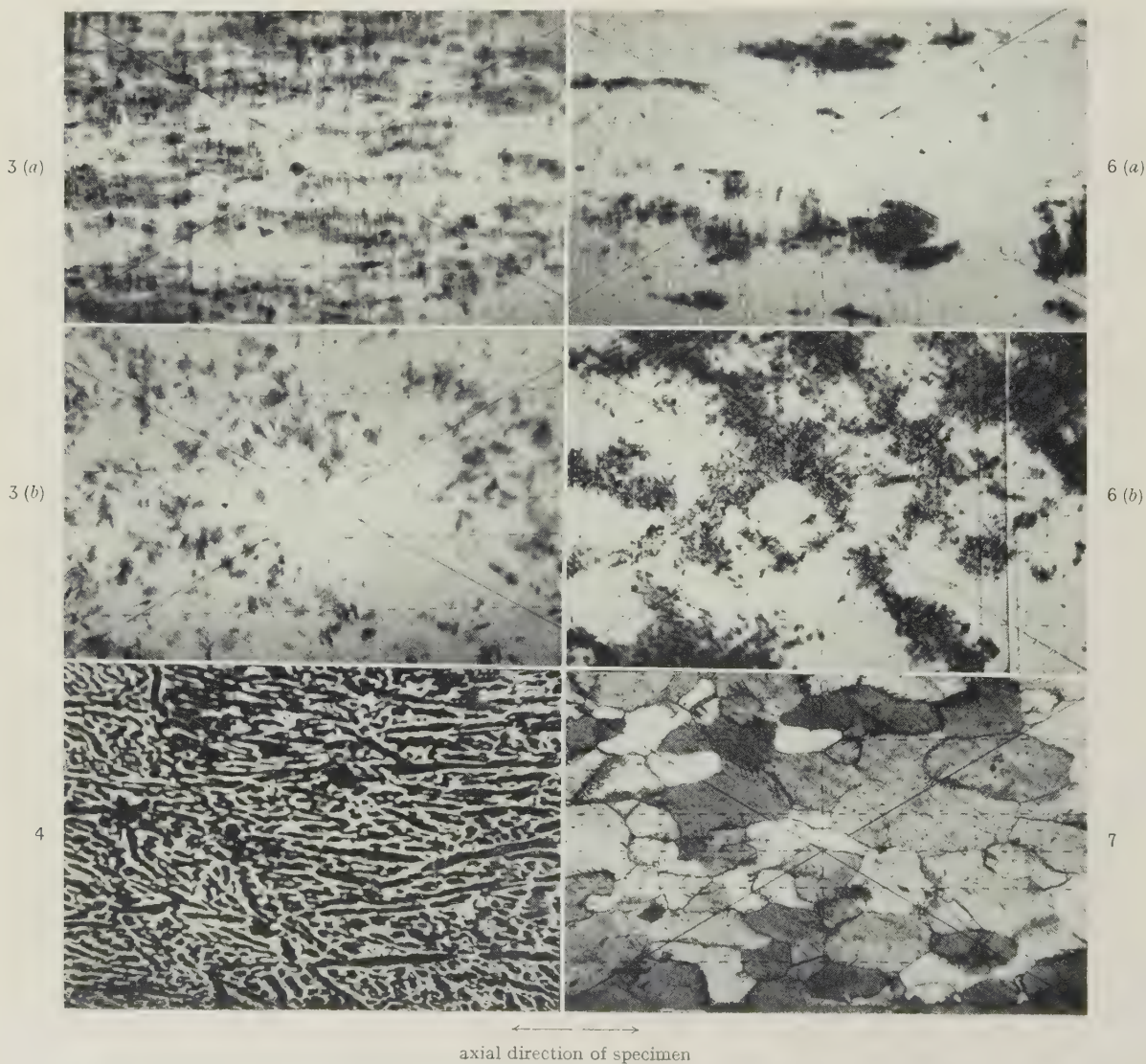


FIG. 3.—Micrograph of the Flecks on an  $(\alpha + \beta)$  Brass Test Specimen: (a) Torsion; (b) Rotating Bending.  $\times 17$ .

FIG. 4.—Micrograph of Crystal Grains of  $(\alpha + \beta)$  Brass.  $\times 17$ .

FIG. 6.—Micrograph of the Flecks on an  $\alpha$ -Brass Test Specimen: (a) Torsion; (b) Rotating Bending.  $\times 17$ .

FIG. 7.—Micrograph of Crystal Grains of  $\alpha$ -Brass.  $\times 17$ .



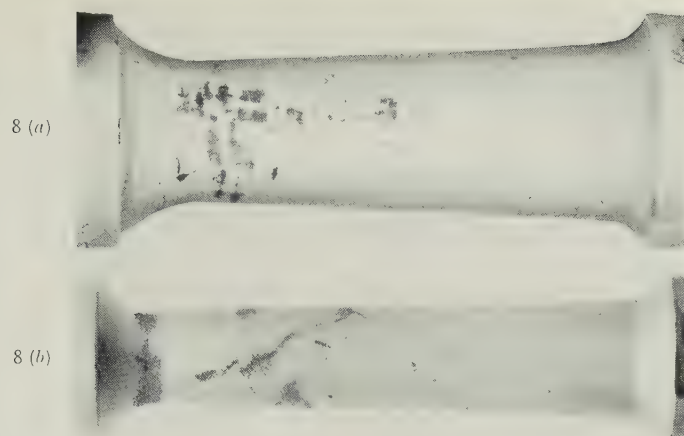


FIG. 8.—Strain Figure Appearing on the Surface of Electroplated Copper on Sand-Cast 6% Tin Bronze : (a) Torsion; (b) Rotating Bending.

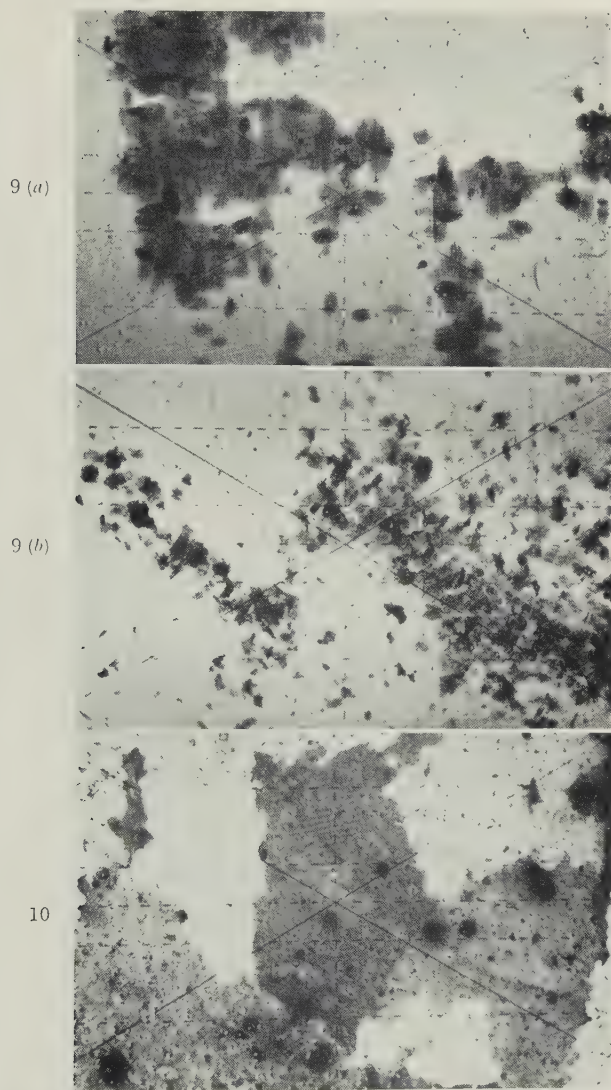


FIG. 9.—Micrograph of the Flecks on Sand-Cast 6% Tin Bronze : (a) Torsion; (b) Rotating Bending.  $\times 17$ .

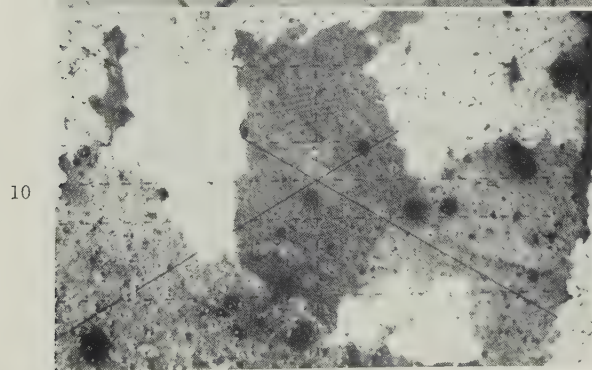
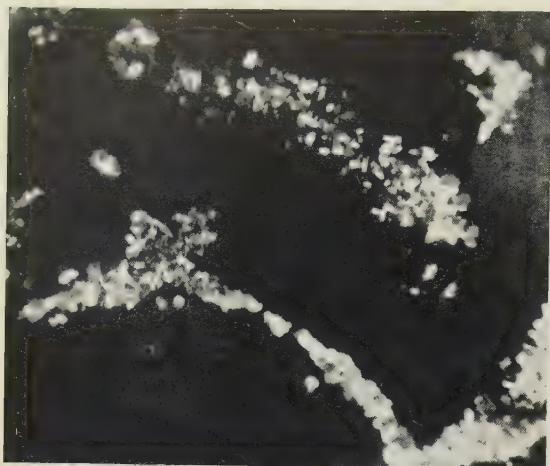


FIG. 10.—Micrograph of Crystal Grains of Sand-Cast 6% Tin Bronze.  $\times 17$ .

← axial direction of specimen

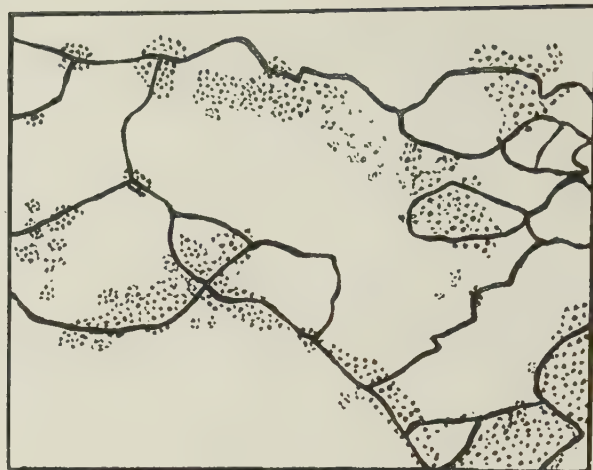
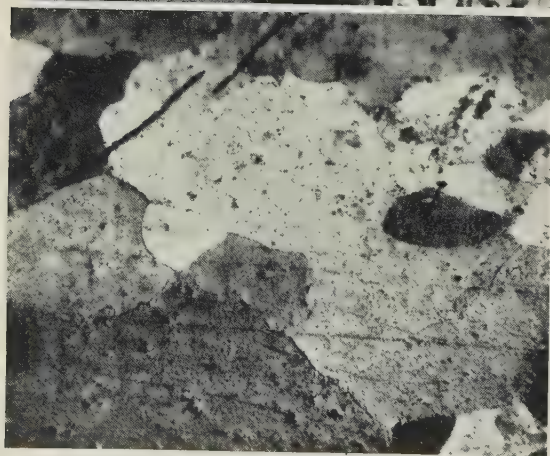
11 (a)



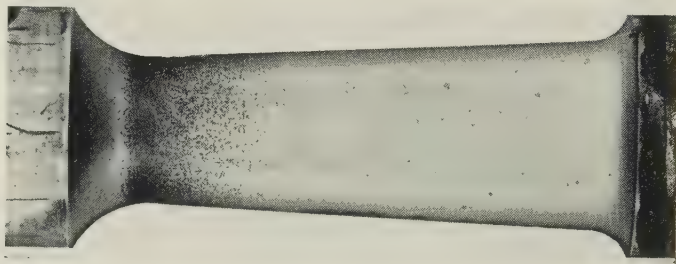
11 (b)



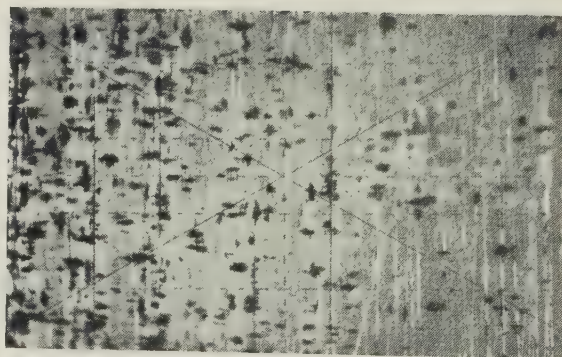
11 (c)



12



13



14

← axial direction of specimen

FIG. 11.—Removal of Copper Deposits from the Test Specimen by Electropolishing: (a) Before Electropolishing; (b) About Half Polished; (c) the Copper Deposits Removed.  $\times 27$ .

FIG. 12.—Relative Position of the Flecks to the Crystal Grains of the Basis Metal. Grain boundaries of the basis metal are represented by full lines and the positions on which the flecks occurred are represented by the dotted area.

FIG. 13. Strain Figure Appearing on the Surface of Electroplated Copper under Repeated-Torsion Test of 0.9% Carbon Steel Specimen.

FIG. 14.—Micrograph of the Flecks on Test Specimen of 0.9% Carbon Steel under Repeated-Torsion Test.  $\times 17$ .



# THE ROLE OF STATISTICAL METHODS IN CONTROLLING THE QUALITY OF NON-FERROUS CASTINGS \*

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By A. R. MARTIN,† B.Sc., A.R.S.M., MEMBER

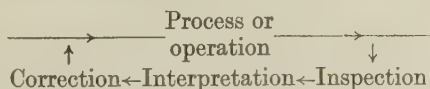
## SYNOPSIS

The paper aims at bridging the gap between foundry practice and the standard text-books on statistical methods of process control. Those methods suitable to foundry purposes are discussed, and a consideration of conventional ways of treating and presenting test data is used to lead up to worked examples showing how the appropriate statistical approach is selected and the results which may be expected from its application.

## I.—INTRODUCTION

THERE are many advantages to be gained from adopting the statistical approach to inspection and control problems in the foundry. Aircraft designers are making considerable use of such methods in digesting the data on which their calculations are based, and also from the design standpoint, while inspection authorities are fully alive to their value in solving the problems with which they are confronted. However, when it is suggested that statistical methods might be applied in the foundry, the objection is usually raised that the information required for control purposes can be obtained from metallurgical examination of the components, but not by a statistical examination of test results. Furthermore, the term "quality control" is apt to suggest inspection by sampling associated with control charts,<sup>1</sup> and while such techniques are suited to many branches of industry, their application is by no means universal.

Error-actuated control, which was discussed by Dr. Singer in a paper submitted to an earlier symposium,<sup>2</sup> is capable of application in the foundry because the operations are not continuous, and the block diagram below suggests the most suitable form :



The load on the inspection department can be reduced by the application of quality-control (sampling) methods, and the interpretation of data can be rendered more effective by the use of statistical methods. There is no suggestion that statistical methods can replace the usual form of interpretation, any more than sampling methods replace inspection.

The primary object of the paper is to demonstrate the role that statistical methods can usefully play in facilitating the correct interpretation of the information provided by inspection records. A secondary object is to furnish illustrations of the way in which such methods may be used to sift the production data on which systems of control are to be based.

## II.—SCOPE OF STATISTICS

For the purpose of foundry control, the term "statistics" may involve nothing more than the collection of test results for presentation in the form of tables or charts. No calculations are involved, but the process represents an attempt to make intelligent use of information. A diagrammatic representation will usually convey far more to the production personnel than tables of figures. Moreover, the work of preparing charts is considerably less than that involved in calculations, and the most vital aspect of control is that it should be rapid. The less tedious the preparation, the more chance the system has of working effectively, and a simple system that provides limited information quickly is of practical value, whereas an elaborate case history is of theoretical interest only.

Mathematical statistics is essentially a study of variation and of probabilities. By statistical methods one can separate causes of variation; once separated, they may be readily identified by other means. It is also possible to define the likelihood of an event being attributable to chance or to some specific cause, and so to distinguish between real and apparent changes.

### 1. PARAMETERS

A parameter is simply a number describing a group of results. The average of the group may rightly be regarded as a parameter because it is typical of the level of the results in the group. Just as the average is a convenient expression of the level of the results, so other parameters may be calculated to provide a convenient expression (or expressions) of the scatter of the results about their mean value.

The measurement of scatter is a concept that forms the basis of control-chart techniques. It also forms the basis of the tests for significance and correlation. Several distributions have been derived from theoretical considerations of the ways in which scatter may take place, the three most frequently used being the Binomial, the Gaussian (normal curve of errors), and the Poisson.

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The Binomial distribution is used when the attribute measured is not continuously variable, e.g. the number of defective castings in a sample.

The Gaussian distribution, which may be regarded as a modification of the Binomial, is used when the attribute measured is continuously variable, e.g. the U.T.S. of a test-piece.

The Poisson distribution is used when the attribute measured may be regarded as the occurrence of an infrequent event, e.g. the occurrence of defective castings in a batch when the expected rate of rejection is of the order of 1 or 2%.

Of the three, the Gaussian distribution is probably the most widely employed. Not only does it describe the pattern expected of random variations in measured properties, but it is fundamentally allied to control-chart techniques. Sampling theory depends on the variation in the material being sampled following the normal curve.

There are several methods of depicting scatter graphically, but that most frequently used is quite similar to the method of illustrating the results of a screen analysis of a sand, and typical analyses are illustrated in Figs. 1 (a) and (b). The mesh sizes of the screens are marked along the horizontal axis, and the vertical heights of the columns are proportional to the percentages retained on

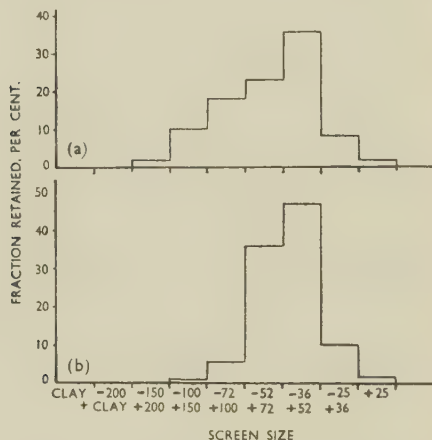


FIG. 1.—Illustrating Screen Analyses of Sands. (a) Congleton sand; (b) Chelford sand (coarse grade).

the various sieves. This method of presenting data will be familiar to foundrymen. Frequency distributions are prepared in the same manner.

#### (a) Standard Deviation

This parameter is a value typical of the deviation of the results in a group about their average value. Algebraically, the sum of these deviations would be zero, but, by ignoring the signs, a mean deviation could be obtained. However, this mean deviation does not bear a simple relationship to the normal error curve.

The signs of the deviations may be eliminated by squaring the individual deviations. These are added to produce a sum of squares, and from this a mean square (instead of a mean deviation) is obtained. In order to reduce the mean square (otherwise called the variance)

to the same dimensions as the measurements from which it was obtained, it is necessary to take the square root, and the root mean square deviation is known as the standard deviation (S.D.). The justification for the extra calculation involved is that the standard deviation does bear

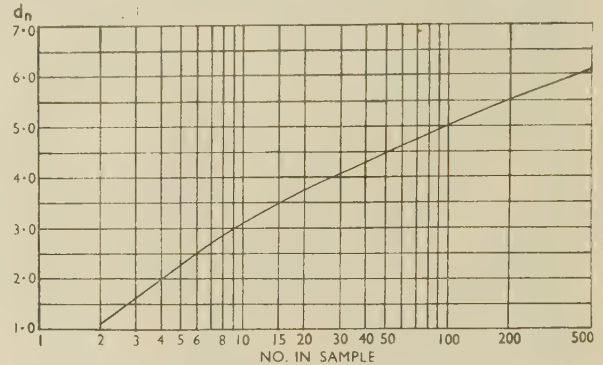


FIG. 2.—Relationship Between  $d_n$  and Sample Size.

$$\text{S.D.} = \frac{\text{mean range}}{d_n}$$

a simple relationship to the normal error curve. For example, 68% of the area contained under the curve is included within a range of  $\pm 1$  standard deviation from the mean. 95.0% of the results will be included within a range of  $\pm 2 \times \text{S.D.}$  and 99.7% within a range of  $\pm 3 \times \text{S.D.}$ , and these are the ranges normally employed on control charts.

This relationship between the standard deviation and the range of the results within the sample is a useful property. Not only may the expected range be predicted from the calculated standard deviation, but the standard deviation may be estimated from the observed range. In this latter case the observed range is divided by a factor  $d_n$  which is related to the sample size, as illustrated in Fig. 2. The estimate obtained from the range of a single sample will not be reliable, and it is more usual to take the average of the ranges of five or ten samples. The factor  $d_n$  is still governed by the number of results in the individual samples and is not influenced by the number of samples.

#### (b) Coefficient of Variation

This quantity is obtained by dividing the standard deviation of the property by the average level and multiplying by 100 to convert to percentage. It may be characteristic of a particular property such as the U.T.S. obtained on making a tensile survey of actual castings.

#### (c) Standard Error of the Average

Just as the individual measurements in a sample are inaccurate estimates of the sample average, so the averages of several samples may be regarded as inaccurate estimates of the true average of the population (from which the samples were drawn). Naturally, the variation expected of the sample averages will be smaller than the variation of the individual results from which they were derived. To obtain an estimate of the standard error (S.E.) of the sample average, the standard deviation of the individual results is reduced by a factor  $\frac{1}{\sqrt{N}}$ , where  $N$  is the number of results in the sample.



Limits of  $\pm 2 \times$  or  $\pm 3 \times$  S.E. may be applied to the average in just the same way as limits of  $2 \times$  or  $3 \times$  S.D. are applied to individual results.

## 2. SIGNIFICANCE TESTS

Large differences supported by large numbers of results do not need a test to measure their reality. But as the difference measured becomes smaller and less obvious and the amount by which the one set of measurements overlaps the other is less easy to define, then, without the aid of a test for significance, no certain conclusion may be drawn.

All significance tests are basically of the same type. A hypothesis is made and a parameter is calculated from the data using the hypothesis. The probability of obtaining such a value by chance is then determined. Three special forms of significance test are available, depending on whether a difference in levels is being measured, or whether the scatter of the values in two groups of results is being compared, or whether the frequency of occurrence of events is being investigated.

### (a) Student's *t*-Test

Student's *t*-test is used for testing the reality of the difference between the averages of two groups of results.

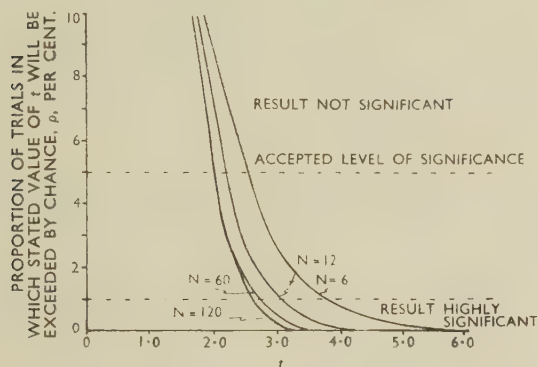


FIG. 3.—Relationship Between *t* and  $\rho$  for 6, 12, 60, and 120 Degrees of Freedom.

Only two groups of results can be tested together, but the number of results in each group need not be the same.

Essentially, the value of *t* is the ratio of the difference between the averages, to the standard error of this difference. In making the test, it is assumed that the two groups of data being considered are actually two samples drawn from the same population. This implies that the variances of the two groups of results will be similar. If the assumption is true, then it is likely that small values of *t* will frequently occur by chance, but that larger values will be obtained much less frequently by chance. The values of *t* taken from "Industrial Experimentation" (Appendix, Table I) are presented in graphical form in Fig. 3. The larger the number of results, the smaller is the likelihood of their being arranged in a given pattern by chance.

### (b) Variance Ratio

To compare the scatter in two sets of results, the variances are obtained and, in the simplest form of test,

the ratio of the larger to the smaller is calculated. In making the test, it is assumed that the results under consideration represent two samples withdrawn from normally distributed populations of the same variance. Again, if the assumption is correct, then values of variance ratio approaching 1 will be obtained frequently by chance. The values of variance ratio taken from "Industrial Experimentation" (Appendix, Table III) are presented in graphical form in Fig. 4.

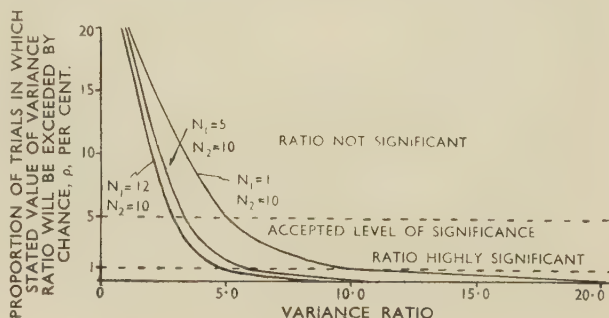


FIG. 4.—Relationship Between Variance Ratio and  $\rho$  for:  $N_1 = 1$ ,  $N_2 = 10$ ;  $N_1 = 5$ ,  $N_2 = 10$ ; and  $N_1 = 12$ ,  $N_2 = 10$  Degrees of Freedom.

### (c) $\chi^2$

Very often, a knowledge of the pattern behind the occurrence of events is required, either in order that their frequency of occurrence may be predicted (e.g. the form of a frequency distribution), or to discover any systematic cause for the pattern (such as a greater incidence of defective castings on a particular shift.)

In either case the accuracy of fit of the actual results with those expected from the assumed pattern may be checked by means of the  $\chi^2$ -test. The difference between each actual result and its corresponding ex-

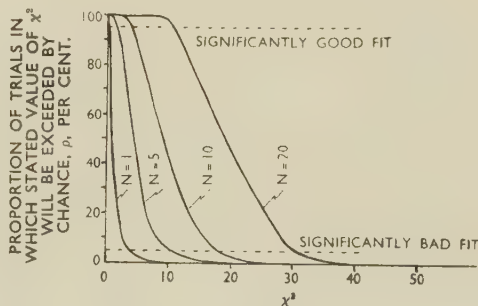


FIG. 5.—Relationship Between  $\chi^2$  and  $\rho$  for 1, 5, 10, and 20 Degrees of Freedom.

pected result is squared, and this quantity is divided by the expected frequency.  $\chi^2$  is the sum of these quantities.

A small value of  $\chi^2$  indicates good agreement and, as the fit becomes progressively worse, so the value of  $\chi^2$  increases. This test becomes unreliable when frequencies of less than 5 are involved. Values of  $\chi^2$  taken from "Industrial Experimentation" (Appendix, Table II) are presented in graphical form in Fig. 5.

## (d) Interpretation of the Test Result

In each of these tests for significance, an assumption is made, and this assumption is verified or refuted by referring the value of  $t$  or variance ratio or  $\chi^2$  to the appropriate table. From these illustrations it is obvious that there is a continuous transition from the likelihood that the arrangement of the results being tested could easily arise by chance (test result not significant) to the likelihood that the results have been arranged by some systematic cause in the pattern obtained (test result significant).

It is generally agreed that, if by chance arrangement of the results being tested the value of  $t$  or variance ratio or  $\chi^2$  would be obtained only once in 20 trials, then the test result may be regarded as significant, and the difference measured may be assigned to some systematic cause. But this is quite obviously an arbitrary choice, and there is a strong case for exercising discretion. It is for this reason that the tables<sup>3</sup> from which Figs. 3, 4, and 5 were drawn quote levels of probability other than the generally accepted 5% (1 trial in 20) level.

## 3. CORRELATION

The final technique to be considered in relation to the scope of this paper is that of correlation. In its simplest

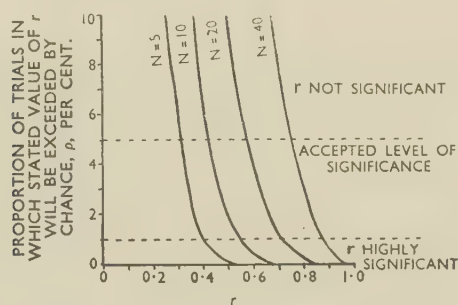


FIG. 6.—Relationship Between Correlation Coefficient  $r$  and  $p$  for 5, 10, 20, and 40 Degrees of Freedom.

form, correlation measures the linear part of the association between two sets of related measurements. A line is determined which makes the sum of squares of the deviations of the individual  $x$  values from the line a minimum. This is called a regression line—in this case the regression of  $x$  on  $y$ . A second line is then determined assuming  $y$  to be the dependent variable (regression of  $y$  on  $x$ ). In an ideal relationship these lines coincide, and in a case of complete dissociation they would lie at right angles. The values of the correlation coefficient obtained from "Industrial Experimentation" (Appendix, Table IV) are presented in graphical form in Fig. 6. This follows the pattern set by the significance tests. The ability to place confidence limits about a regression line is of considerable value, especially when relationships are derived from large masses of production data. For example, if as few as 22 pairs of results are correlated, a coefficient as low as  $r = 0.4$  may indicate a significant relationship. The residual variation is obtained by multiplying the standard deviation of the dependent variable by  $\sqrt{1 - r^2}$ . In the case just quoted  $\sqrt{1 - r^2} = 0.92$ , and the relationship, although valid, is of little value for control purposes. It is also

important to see that the relationship is linear, as otherwise the simple formula given in the references<sup>3, 5</sup> does not apply.

## III.—CONTROLS APPLIED IN THE FOUNDRY

## 1. GENERAL INTRODUCTION

At the melting stage, control over the melt composition is exercised by the charge calculator and the analytical laboratory. Control of the treatment of the melt is usually measured in terms of the tensile properties of separately cast test-pieces or by assessment of grain-size checks or gas-content checks. Casting techniques are normally criticized in terms of the visual-inspection or radiographic-inspection reports or on the basis of fracture tests, actual loading tests, or by other means of assessing the serviceability of the components.

Control over the properties of moulding and core sands may also be exercised by measuring such quantities as permeability, compression strength, and moisture content.

In the following sections, the factors involved in establishing control are examined in detail. The objects of the system are stated, and conventional methods of presenting the data are demonstrated.

The appropriate statistical approach is determined in the first instance by whether the process is being controlled by measurements of properties such as tensile strength, composition, or permeability, or whether it is being controlled by assessment of attributes such as the presence or absence of casting defects.

The data to be entered on control charts must be considered in relation to the accuracy of the measurements being made; the nature of the "batch" from which the samples are to be drawn must also be taken into account.

If a property can be measured accurately, only one measurement is required to provide a reliable estimate, e.g. a dimension measured with a micrometer. If, however, the method of measurement is known to be inaccurate for any reason, then several such measurements have to be made and their average taken in order to provide a more reliable estimate. For example, a single test-piece cut from a casting does not provide an accurate estimate of the strength of the casting as a whole.

If individual measurements provide reliable estimates of the property being measured, then the individual results may be plotted between control limits based on the standard deviation. For example, separately cast test-pieces provide a reliable estimate of melt quality, and only one need be tested for each batch of metal treated.

Where several melts are treated (and tested) during the course of the day, it may be preferred to plot the daily average of the tensile properties to give a clearer indication of the day-to-day variation, and, because averages are plotted, the control limits will be based on the standard error of the average. But in such a case the grouping is quite artificial, for the day's work is regarded as a batch, and this is not true in the metallurgical sense.

If batch charges are made to a continuous-melting furnace, the composition of the metal drawn from the



furnace may fluctuate during the course of the day. Samples taken during the day can be analysed to determine the extent of the variation, and the order of the variation indicated by plotting the standard deviation of the day's analyses or, more simply, the range. The limits for the range are based on the standard deviation of the range. Day-to-day variation is indicated by plotting the averages obtained from the day's analyses between limits based on the standard errors of the averages. In this case the day's work may more justifiably be regarded as a batch.

## 2. CONTROL BY CHEMICAL ANALYSIS

### (a) Factors Involved

The calculated content of an element provides a reference and a criterion of control. Small variations in composition (causing a small scatter about the values expected from the charge calculation) may be expected to arise from:

- (i) Minor errors in charge weighing.
- (ii) Variations in the composition of the components of the charge.
- (iii) Loss or gain during remelting and/or holding.
- (iv) Mixing the charge.
- (v) Variation in the analytical method (and sensitivity of the method to operator technique).

Over and above these random variations, there may be systematic trends associated with:

- (vi) Progressive loss or gain of an element.
- (vii) Zero drift or some other bias in the analytical method.

### (b) Objects of Control System

The purpose of the control system will be:

- (1) To indicate the order of the scatter expected under normal working conditions and to determine the reliance that can be placed on the calculated values.
- (2) To separate systematic trends and to locate their cause.
- (3) To draw attention to the frequency with which rogue results (attributable to carelessness either in the foundry or in the laboratory) occur.

### (c) Conventional Treatment

The simplest form of control consists in plotting the compositions of consecutive melts. If several melts are analysed each day, it may be preferable to plot the daily average or to plot the range of the results, or both.

The values expected from the charge calculation may be entered on the chart so that departures from them become instantly recognizable. Consistent departures from the expected values will indicate pick-up or loss. An illustration based on alloy LM16 is given in Fig. 7.

Changes in charge constitution (change in batch of hardener alloy or supplier of secondary alloy ingot, &c.), alterations in type of melting furnace, and any other factors likely to introduce variation should be noted on such charts. If shift work is involved, then the changes in shifts should be given, or it may be preferable to run a separate chart for each shift.

### (d) Example of Statistical Methods

Analytical results for copper, silicon, and iron contents have been extracted from records for D.T.D. 304A

alloy, and the difference between the actual value obtained and the value predicted from the charge calculations is expressed as a loss or gain factor in Table I. The differences between the expected and

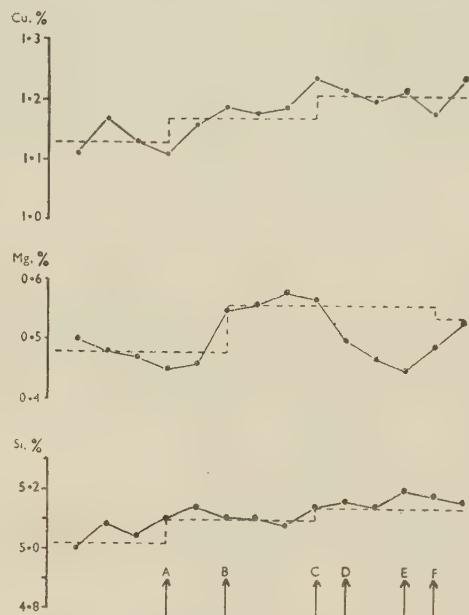


FIG. 7.—Charts Showing Changes in Chemical Composition of LM16 Alloy. Calculated charge is shown in broken lines.

Arrow A : Cu-Si hardener. Batch ref. A.D.H.  
 „ B : Mg hardener. Batch ref. M.O.T.  
 „ C : Cu-Si hardener. Batch ref. A.D.L.  
 „ D : Change to reverberatory melting.  
 „ E : Mg loss corrected to restore level.  
 „ F : Mg hardener. Batch ref. M.O.U.

TABLE I.—Application of Statistical Methods to Charge Constitution of D.T.D. 304A Alloy.

Copper		Silicon		Iron	
Gain or Loss	Frequency of Occurrence	Gain or Loss	Frequency of Occurrence	Gain or Loss	Frequency of Occurrence
+0.2	1	+0.05	1	+0.12	1
+0.1	3	+0.04	1	+0.11	1
0	8	+0.03	4	+0.10	0
-0.1	13	+0.02	5	+0.09	2
-0.2	22	+0.01	20	+0.08	1
-0.3	18	0	33	+0.07	1
-0.4	8	-0.01	13	+0.06	2
-0.5	6			+0.05	7
-0.6	0			+0.04	8
-0.7	1			+0.03	15
				+0.02	14
				+0.01	15
				0	7
				-0.01	4
				-0.02	1
				-0.03	1

actual values for copper content have been corrected to the nearest 0.1%. The silicon and iron values did not need correcting.

In order to obtain a visual assessment of the scatter, frequency distributions of the loss or gain factors have

been drawn up for the three elements. The frequency distribution for copper (Fig. 8 (a)) is slightly skew, but does not differ significantly from a normal distribution with the same average and standard deviation. It indicates a quite definite loss of copper on remelting. The distribution for silicon (Fig. 8 (b)) is markedly skew, suggesting a high probability that silicon will be neither picked up nor lost and that the variation is extremely small, but that occasionally silicon may be picked up in appreciable amounts. Attention to detail could

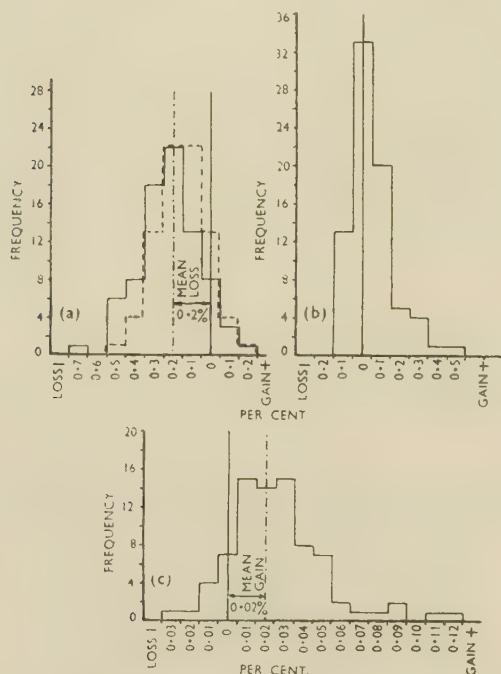


FIG. 8.—Frequency Distributions of Loss and Gain Factors of Elements in Melting D.T.D. 304A Alloy. (a) Copper; normal distribution superimposed in broken lines. (b) Silicon. (c) Iron.

eliminate this "tail" from the frequency distribution. The distribution for iron (Fig. 8 (c)) demonstrates that loss or gain in iron content is more variable and clearly indicates a consistent iron pick-up at each remelting. The slightly skewed distribution suggests that whilst the pick-up is reasonably consistent, it may on occasions be much worse. The state of affairs for the two impurities silicon and iron is more or less exactly what might have been supposed from a knowledge of the working conditions.

The loss of copper and pick-up of iron may be judged to be real effects by visual assessment of the frequency distributions, and there is no point in carrying out any test for significance.

If it were considered that the copper content is critical and should be maintained within closer limits than those laid down by the specification, then limits based on  $\pm 2 \times \text{S.D.} = \pm 2 \times 0.17 = \pm 0.34\%$ , could be applied, as illustrated in Fig. 9.

In the case of impurities, control limits will not normally be required, but it may be desired to run with an impurity close to the maximum permitted by the specification. In such a case it would be more to the

point to plot a control limit below the maximum permitted by the specification; the calculated content should not exceed this level. This has been done for the iron content (see Fig. 9).

In the case just considered, a visual assessment of the scatter of the results was sufficient to suggest that the loss of copper and pick-up of iron were real effects. In relation to loss or gain values for the magnesium content of L53 alloy, listed in Table II, it is difficult to say whether an allowance should be made for a systematic loss without recourse to a test for significance. The appropriate test in this instance is the *t* test.

TABLE II.—Frequency Distribution of Loss and Gain Factors of Mg in Melting L53 Alloy.

Loss or Gain, % (1)	Frequency of Occurrence (2)	(1) <sup>2</sup> (3)	(2) × (1)	(2) × (3)
+0.5	1	0.25	+0.5	0.25
+0.3	4	0.09	+1.2	0.36
+0.2	9	0.04	+1.8	0.36
+0.1	12	0.01	+1.2	0.12
0	13	0	0	0
-0.1	9	0.01	-0.9	0.09
-0.2	14	0.04	-2.8	0.56
-0.3	9	0.09	-2.7	0.81
-0.4	3	0.16	-1.2	0.48
-0.5	4	0.25	-2.0	1.00
-0.6	1	0.36	-0.6	0.36
-0.8	1	0.64	-0.8	0.64
<i>n</i> = 80			<i>Sx</i> = -6.3	<i>Sx</i> <sup>2</sup> = 5.03

$$\bar{x} = \frac{Sx}{n} = -0.80$$

$$\frac{(Sx)^2}{n} = 0.4961$$

$$Sx^2 - \frac{(Sx)^2}{n} = 4.5331$$

$$\text{Variance} = \frac{4.5331}{79} = 0.0573$$

$$\text{S.D.} = \sqrt{\text{Variance}} = 0.239$$

So that

$$t = \frac{0.80}{0.239} \times \sqrt{80} = 2.992$$

This value of *t* lies between those quoted for the *p* = 0.01 and *p* = 0.001 levels. This result is quite significant and confirms that allowance should be made for a melting loss of 0.1%.

The conditions investigated yielded a standard deviation of 0.24%. Most foundries casting this alloy prefer to run with the magnesium content as near the maximum permitted by the specification as possible, in order to be sure of maintaining the highest level of tensile properties. If, in these circumstances, the maximum of 11.0% is not to be exceeded, the calculated magnesium content should not be higher than  $11.0 - 3 \times 0.24 = 10.3\%$ , although if the founder concerned was prepared to take the risk that  $2\frac{1}{2}\%$  of his melts might exceed the specified maximum, the calculated level could be raised to  $11.0 - 2 \times 0.24 = 10.5\%$ .



(e) *Evaluation of Chemical Analysis by Statistical Methods*

If several operators make estimates by a standard or reference method and by an alternative method under investigation, the results can then be compared graphically for possible obvious differences; bias, &c., and statistical methods applied to compare the variation within the methods.

In its more elaborate form, the technique of analysis of variance is extremely useful in developing spectrographic methods, where the possible sources of variation are the sample, the emulsion of the photographic plate,

Systematic trends in tensile properties may arise from such factors as :

(a) Progressive build-up of chemical impurities.

(b) Progressive increase in grain-size due to the recirculation of process scrap derived from castings poured at high temperatures.

(c) Progressive increase of non-metallic inclusion content due to the recirculation of process scrap.

Wide variations in the properties may usually be assigned either to casting defects occurring in the gauge-length of the test-bar casting, or to incorrect treatment of the melt, or to incorrect heat-treatment.

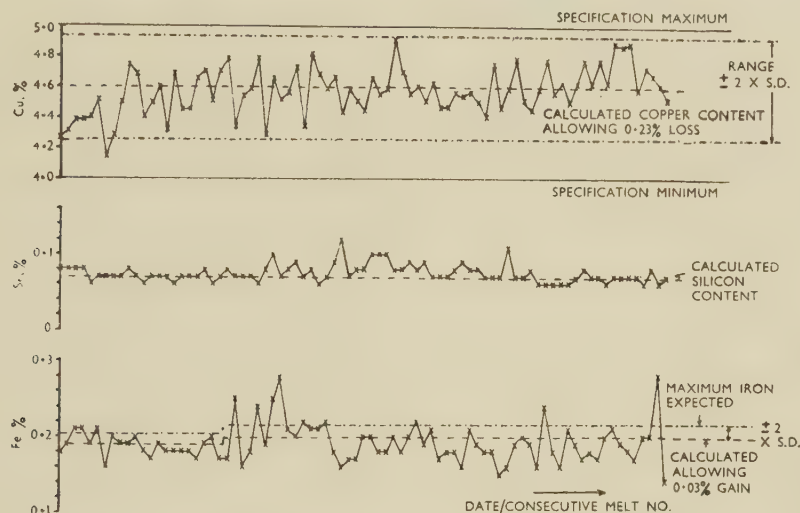


FIG. 9.—Control Chart Based on Chemical Analysis for D.T.D. 304A.

the processing of the plate, and reading of the micro-photometer.

### 3. CONTROL BY TENSILE PROPERTIES

#### (a) *Factors Involved*

In analytical control there is an accurately predictable expected value against which the actual value obtained may be compared. Melt quality, as determined by test-bar properties, may be judged effectively only in terms of past experience, a fact that immediately suggests a statistical approach.

Factors influencing the tensile properties of castings are :

- (i) Chemical composition.
- (ii) Gas content.
- (iii) Grain-size.
- (iv) Non-metallic inclusion content.
- (v) Feeding conditions.
- (vi) Heat-treatment.

Small random variations in the test-bar properties will result from minor fluctuations in all the above conditions. For this reason it is essential that the design of the test-bar casting and its gating and riser system should be such that variations in feeding conditions will be at a minimum. Unless this is so, it will be impossible to judge the effects of other factors without recourse to the analysis of variance.

The purpose of the control system is :

- (1) To indicate the degree of consistency in the working conditions by the range of the control limits and by the number of results lying between the control limits.
- (2) To define systematic trends.
- (3) To draw attention to results falling outside the limits (calling for a metallurgical examination of the material) and to the frequency with which they occur.

#### (b) *Conventional Treatment*

As with the results of chemical analyses, simple graphs, in this case of U.T.S. and percentage elongation, may be plotted on a consecutive-melt basis. Notes should be included on such graphs of the scrap content of the charge, changes of melting equipment or in metal treatment, and any other factors likely to influence the properties.

#### (c) *Examples of Statistical Methods*

The graphs may be elaborated by adding control limits based on the standard deviation for individual results or on the standard error for results grouped and averaged.

Although erratic low results may be thought of as being due to chance causes, they are nevertheless quite real effects and may justifiably cause rejection of the "batch" they represent. For this reason it would not be advisable to attempt to use sampling techniques, as

such techniques depend on the material being homogeneous.

The data on which control limits are to be based should be carefully criticized and, as a first step, the test results can conveniently be drawn up in the form of a frequency distribution to obtain a clear overall picture of the scatter. There may be metallurgical reasons why the distribution should differ from normality and, if no account is taken of these reasons, the control limits will be useless. For example, during the period in which the results were collected they may have been influenced by a systematic trend. Alternatively, the frequency distribution may exhibit a marked "tail", indicating that whilst the treatment is successful in the main there is obviously scope for improvement.

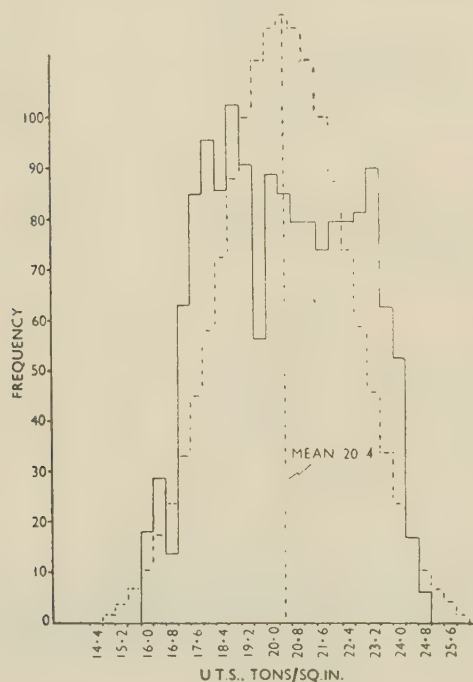


FIG. 10.—Distribution of 1550 Check-Test Results for U.T.S. of LM10 Alloy. Normal distribution having same mean and S.D. superimposed in broken lines.

When the response to treatment of the alloy is considerable, it is possible that the picture presented by the non-normal frequency distribution will be the summation of two or more distributions, each representing a different level of control.

This latter set of circumstances is illustrated by the frequency distribution of Fig. 10, which is based on approximately 1550 test results obtained from sand-cast test-pieces in L53 alloy. The picture presented may be taken as typical of the conditions with which a founder may be faced when attempting to fix control limits for an unfamiliar alloy, and the statistical approach in this instance is to attempt to break the overall distribution down into its component distributions and to check the accuracy of the synthetic (expected) frequencies against the actual by means of the  $\chi^2$  test. For convenience in working, the U.T.S. values have been grouped in intervals of 0.4 ton/in.<sup>2</sup>.

For comparison, a normal distribution having the same mean of 20.4 tons/in.<sup>2</sup>, standard deviation (S.D.)

of  $\pm 2.0$  tons/in.<sup>2</sup>, and number of results, has been superimposed in broken line on the distribution of the U.T.S. values in Fig. 10. The expected frequencies for this distribution have been approximated from tables of the ordinates of the normal curve and are listed as distribution A in Table III. Frequencies below 5 at the tails

TABLE III.—Frequencies for Distribution of U.T.S. Values in LM10 Alloy.

U.T.S. Interval,* tons/in. <sup>2</sup>	Actual Frequency	Expected Frequency		
		A	B	C
16.0	18	11	14	12
16.4	29	17	21	25
16.8	14	24	35	44
17.2	65	34	57	67
17.6	85	46	80	87
18.0	97	59	91	99
18.4	87	74	82	99
18.8	104	89	65	111
19.2	92	102	57	83
19.6	57	113	63	78
20.0	90	120	78	78
20.4	86	122	87	81
20.8	80	120	78	82
21.2	80	113	63	78
21.6	74	102	57	71
22.0	80	89	65	66
22.4	80	74	82	74
22.8	82	59	91	91
23.2	91	46	79	96
23.6	63	34	54	75
24.0	53	24	29	43
24.4	17	17	12	18
24.8	16	11	5	4

\* For convenience in working, the U.T.S. values have been grouped in intervals of 0.4 ton/in.<sup>2</sup>.

TABLE IV.—Stages of Calculation of  $\chi^2$  for U.T.S. Values in LM10 Alloy.

Actual Frequency	Expected Frequency A	Difference	(Difference) <sup>2</sup>	(Difference) <sup>2</sup> / A
18	11	7	49	4.5
29	17	12	144	8.5
14	24	10	100	4.2
65	34	31	961	28.3
85	46	39	1521	33.1
97	59	38	1444	24.5
87	74	13	169	2.3
104	89	15	225	2.5
92	102	10	100	1.0
57	113	56	3136	27.8
90	120	30	900	7.5
86	122	36	1296	10.6
80	120	40	1600	13.3
80	113	33	1089	9.6
74	102	28	784	7.7
80	89	9	81	0.9
80	74	6	36	0.5
82	59	23	529	9.0
91	46	45	2025	44.0
63	34	29	841	24.7
53	24	29	841	35.0
17	17	0	0	0
				299.5

of the distribution have been pooled. The value for  $\chi^2$  has been calculated and the stages of the calculation are detailed in Table IV. The value obtained is 299.5, and clearly there is no association.



From an inspection of the peaks in the frequency distribution of Fig. 10, four distributions have been chosen empirically, and their parameters are listed in Table V.

TABLE V.—Frequency Distribution in U.T.S. Values of LM10 Alloy.

	Distribution No.			
	1	2	3	4
Averages . . . . .	16.0	17.6	20.0	22.8
Peak frequencies . . . .	10	90	85	90
S.D. . . . .	0.8	0.8	0.8	0.8

The frequencies for these distributions have also been approximated from tables for the ordinates of the normal error curve. Where the distributions overlap, the frequencies have been summed, and the overall picture is presented as distribution *B* in Table III. By taking the frequencies of distribution *B* as the expected values,  $\chi^2$  is reduced to 111.55, confirming that a better fit has been achieved, although it is still significantly bad.

By reducing the number of distributions to three and adjusting the levels of the averages, and by adjusting the spread to provide more or less overlap, the fit can be improved still further. The parameters of the three distributions are listed in Table VI. The frequencies

TABLE VI.—Frequency Distribution in U.T.S. Values of LM10 Alloy.

	Distribution No.		
	1	2	3
Mean . . . . .	18.0	20.8	23.2
Peak frequencies . . . .	90	80	80
S.D. . . . .	1.00	1.33	0.67

have been summed to produce distribution *C* in Table III, and are illustrated in Fig. 11.

The overall distribution obtained from these three distributions is entered in broken line on the distribution of the observed results in Fig. 11. In this case the value of  $\chi^2$  has been reduced to 44.12. There are 23 steps of U.T.S. values, so that there will be  $23 - 1 = 22$  degrees of freedom. From the 22 degrees of freedom, a further 6 degrees must be deducted because 6 parameters (3 averages and 3 standard deviations) have been obtained from the data. This deduction must be made in spite of the fact that the parameters have been estimated visually and have not been calculated. For the probability level  $p = 0.05$  and  $22 - 6 = 16$  degrees of freedom, the tables list a value of  $\chi^2$  of 26.3, and to achieve a significantly good fit the value obtained experimentally would have to be equal to or less than this.

Whilst the result still indicates a significantly bad fit at the accepted level of probability, the three distributions chosen obviously produce an overall distribution that is much nearer to the truth, and it is possible that by further refinement an even more accurate fit might be obtained. For control purposes, however, the result

is sufficiently near to the truth to enable working limits to be drawn up. Control limits based on distribution *A* (Table III) and on two of the three distributions listed in Table VI, are drawn up for comparison in Table VII.

TABLE VII.—Control Limits for U.T.S. Values of LM10 Alloy.

	Average U.T.S. tons/in. <sup>2</sup>	S.D.	Control Limits	
			Min., tons/in. <sup>2</sup>	Max., tons/in. <sup>2</sup>
Distribution <i>A</i> (Table III)	20.4	2.0	16.4	24.4
Distributions 2 and 3 (Table VI)	21.6	1.6	18.4	24.8
Distribution 3 alone	23.2	0.8	21.6	24.8

Clearly the limits based on the results taken at their face value (distribution *A*) are useless, since they include both satisfactory and unsatisfactory results. Limits

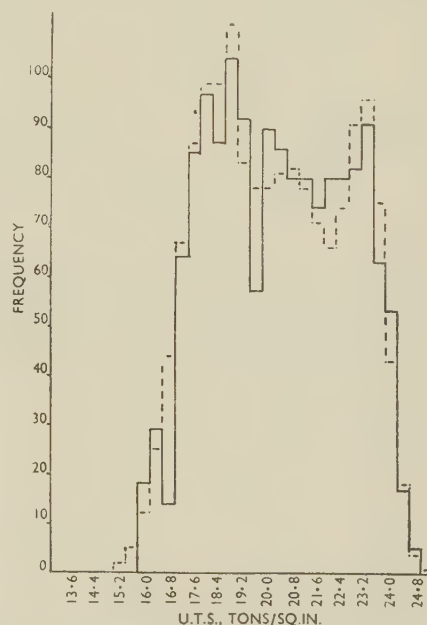


FIG. 11.—Check-Test Results for U.T.S. of LM10 Alloy with Distribution *C* Superimposed.

based on distributions 2 and 3 (Table VI) offer a better criterion of melt quality and limits treated successfully.

In the course of this pruning process, the scatter has been reduced and the average raised, but the top limit has remained sensibly constant.

The justification for introducing an admittedly difficult case is that it emphasizes the danger of taking production data at their face value and illustrates the complications that may arise when information is not collected on an organized basis. A more practical approach would be to collect results from test-bars, cast both before and after treatment, and to assess the reality of the improvement in level by the *t* test or the reduction in scatter by the variance-ratio test. If the treatment brings about a real improvement, control limits may be fixed on the results representing only metal successfully treated.

The frequency distributions for the U.T.S. values obtained from test-pieces cast in 3L33 alloy, both before and after treatment, are listed in Table VIII and illus-

TABLE VIII.—U.T.S. Values Obtained from Sand-Cast D.T.D.-Type Test-Bars of 3L33 Alloy Cast Before and After Treatment.

Before Treatment		After Treatment	
U.T.S., tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>
7.3	6.8	8.4	11.5
10.2	7.5	11.2	11.1
7.4	8.3	11.7	11.7
6.3	7.6	11.2	10.9
5.8	7.4	9.7	11.8
6.8	7.3	11.4	11.7
7.7	8.1	11.5	11.4
7.8	6.9	11.2	11.3
7.2	7.6	10.7	11.2
6.4	8.2	11.1	11.4
8.2	6.5	10.6	12.6
7.1	8.6	10.2	12.2
7.6	8.2	11.2	12.7
7.3	8.6	10.4	12.0
7.3	8.2	11.5	11.6
8.5	7.5	11.6	11.4
8.2	7.6	10.3	11.4
7.7	8.5	10.6	11.3
6.6	7.5	11.5	12.0
8.3	8.3	11.6	11.9
8.0		11.2	

strated in Fig. 12. L33 is an aluminium-12% silicon alloy and is subject to modification either with metallic sodium or with fluxes containing sodium fluoride. This

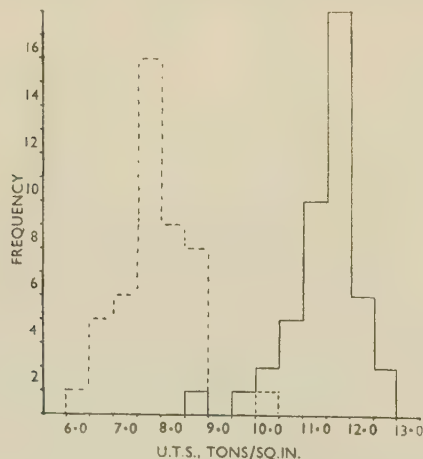


FIG. 12.—U.T.S. Values for 3L33 Alloy as Modified. The values for unmodified metal are superimposed in broken lines.

effects a very marked improvement in both U.T.S. and elongation. Clearly there is no need to test the significance of the difference between the averages of these two distributions, and it merely remains to fix the control limits for the treated metal.

The standard deviation obtained from the U.T.S. values after treatment, listed in Table VIII, is 0.75 ton/in.<sup>2</sup>, and the limits based on the average U.T.S. of 11.3 tons/in.<sup>2</sup> in conjunction with this standard deviation will be  $11.3 \pm 2 \times 0.75$  tons/in.<sup>2</sup>. The individual results

for treated metal from Table VIII have been plotted in Fig. 13 (a) with these control limits entered on the graph.

A better appreciation of long-term trends may be obtained if the control chart is based on the averages

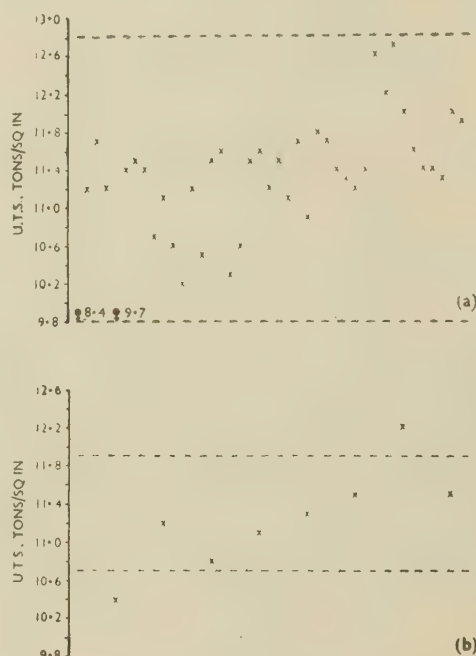


FIG. 13.—(a) Individual Values for U.T.S. of 3L33 Alloy with Control Limits  $\pm 2 \times$  S.D. (b) Samples of 5 Consecutive Test Results for U.T.S. of 3L33 Alloy with Control Limits  $\pm 2 \times$  S.E.

of three, four, or five consecutive melts and the limits fixed on plus or minus twice the standard error. This procedure is illustrated in Fig. 13 (b) for samples of five consecutive melts, the control limits being  $\pm 2 \times \frac{\text{S.D.}}{\sqrt{5}} = \pm 2 \times \frac{0.75}{2.236} = \pm 0.68$  ton/in.<sup>2</sup>.

The slightly skew distribution for the U.T.S. values for treated metal may result in part from the trend apparent in Fig. 13 (a). On both control charts there are points falling outside the limits, and this suggests that tighter control should be possible. This would not have the effect of transferring the distribution as it stands to a higher level, but of leaving the top limit at its existing level and (by correcting the skewness) raising the lower limit which, as it stands, is below the minimum U.T.S. specified.

A rather different state of affairs obtains in the case of the data listed in Table IX and one which requires a different statistical approach. The fact that there is considerable overlap between the U.T.S. values obtained before and after treatment may be inferred from the table of results, but is made clear when composite frequency distributions (Fig. 14) are prepared. The form of the distributions suggests that the value of carrying out the treatment does not in this case lie in raising the average level, but in reducing the scatter. A statistical treatment is thus essential, and in the first place the variances of the treated and untreated metal are compared. The *t*-test may not be applied if the



variances differ significantly. The stages of the calculation are set out in Table X.

TABLE IX.—*U.T.S. Values Obtained from Sand-Cast D.T.D.-Type Test-Bars of D.T.D. 424A Cast Before and After Treatment.*

Before Treatment		After Treatment	
U.T.S., tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>
6.8	9.8	10.4	9.9
7.5	9.7	9.8	9.5
8.8	10.0	9.9	9.7
6.8	10.4	9.6	9.7
9.2	8.5	9.9	9.4
9.5	7.5	10.0	10.3
9.9	10.6	10.6	9.5
10.0	9.4	10.3	9.9
10.3	10.9	10.4	10.6
9.3	10.0	9.2	10.8
9.5	10.1	9.1	9.9
9.0	10.2	10.0	9.8
10.8		10.2	

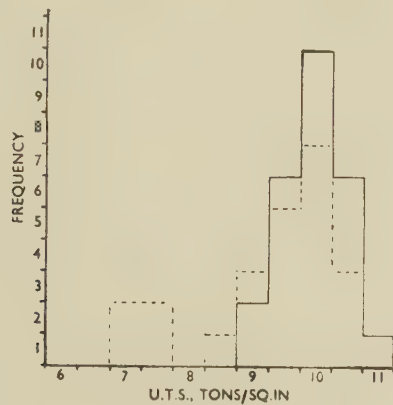


FIG. 14.—U.T.S. Values for Treated Specimens of D.T.D. 424A Alloy. Values for untreated metal superimposed in broken lines.

TABLE X.—*Comparison of Variances of U.T.S. of D.T.D. 424A.*

	Before Treatment	After Treatment
$\Sigma x$	234.5	248.4
$n$	25	25
$\bar{x}$	9.38	9.94
$\Sigma x^2$	2231.91	2472.68
$\frac{(\Sigma x)^2}{n}$	2199.61	2468.1024
$\Sigma x^2 - \frac{(\Sigma x)^2}{n}$ (sum of squares)	32.30	4.5776
Mean square or variance	1.3458	0.1907

The larger variance is divided by the smaller and the ratio referred to the appropriate table.

The variance ratio is  $\frac{1.3458}{0.1907} = 7.0572$ , and there are 24 degrees of freedom for each group. Because it was not known beforehand which of the two variances would be the larger and which the smaller, the probability levels in the tables have to be doubled. The ratio 7.06 is highly significant ( $p = 0.002$ ), confirming that the metal treatment reduces the scatter significantly.

Control limits can be worked out for the distribution representing "good" metal as already illustrated.

#### 4. SAND TESTS

Sand testing involves quantitative measurements of such properties as green and baked compression strengths (or baked tensile strength), permeability, moisture content, &c. These data may be treated along the lines already described in connection with analytical and test-bar property data.

#### 5. HARDNESS TESTS

Hardness testing is widely used as a check on response to heat-treatment and on the uniformity of the response of castings within a heat-treatment load.

In particular, light-alloy piston castings are generally released to the customer to agreed Brinell hardness limits. It is usual to employ a load of 1000 kg. and a 10-mm.-dia. ball. The diameter of the impression is normally read with a microscope provided with a scale calibrated in 0.1-mm. divisions, and consequently it is reasonable to estimate to 0.05 mm. Little would be gained by attempting to estimate to 0.02 mm., and the more practical course is to take the average of a large number of individual estimates and to accept this as a reliable estimate of the hardness of the batch. A control chart, indicating the "between heat-treatment load variation", would be of use in regulating the process. As already suggested, the hardness of the batch can best be obtained as the average of a large number of estimates, and the control-chart limits will therefore be based on the standard error of the average.

At the works with which the author is associated, a heat-treatment load normally consists of 2000 piston castings, and because of the time consumed in hardness testing it is essential to take a sample. In this case the sample is being taken to provide a quantity of inaccurate estimates of the hardness of the batch for the purpose of checking the "between-batch variation" and, in consequence, the sample size may be selected arbitrarily. A sample of 100 castings makes the average easy to calculate and to check the standard error, the standard deviation is divided by  $\sqrt{100} = 10$ .

To collect the information, a card is drawn up as shown in Fig. 15, and by entering a mark in the appropriate square a frequency distribution is obtained. This provides an immediate visual warning of any abnormal "within heat-treatment load" condition. The average value is readily obtained by multiplying each impression diameter by its frequency of occurrence and adding.

The data in Table XI have been collected from 10 consecutive heat-treatment batches:

TABLE XI.—*Brinell Hardness Data from Heat-Treatment Batches of Piston Castings.*

Dia. of Impression, mm.	Frequency of Occurrence:									
	Test No.									
	1	2	3	4	5	6	7	8	9	10
3.0	...	...	...	...	...	...	...	...	...	...
3.05	...	...	6	3	...	...	1	...	...	3
3.1	2	7	24	23	2	3	5	8	...	25
3.15	18	48	29	42	18	26	17	58	39	42
3.2	39	31	36	25	57	60	52	29	49	23
3.25	25	10	4	5	18	11	19	4	12	5
3.3	16	4	1	2	5	...	6	1	...	2
Average dia., mm.	3.22	3.18	3.16	3.17	3.20	3.19	3.20	3.17	3.19	3.15
Sample range	0.20	0.20	0.25	0.25	0.20	0.15	0.25	0.20	0.10	0.25

Date 3-4-56				Heat-Treatment Batch No. D716												Alloy Specn. LM13-WP											
Dia., mm.	Frequency																									Total	Pro- duc-
	1	5	10	15	20	25	30	35	40	45	50																
3-40																											
3-35																											
3-30																											
3-25	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	6	19.5
3-20	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	25	80.0
3-15	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	38	119.7
3-10	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	25	77.5
3-05	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	6	18.3
3-00																											
2-95																											
2-90																											
																									Totals	100	315.0
																									Average		3.15

FIG. 15.—Hardness-Check Record Card.

Final Inspection Record Sheet					Reasons for Rejection									
					Bad Finish	Damaged Mould/Casting	Cross-Jointed	Misplaced Cores	Cold Shuts/Misrun	Oxide Inclusions	Entrapped Air/Blows	Cracked	Shrinkage	Sears
Date	Part No.	No. Cast	No. O.K.	Total Rejected										
3/4/56	Long-Run Jobs													
	A123	15	10	5								5		
	B456	50	48	2					2					
	Short-Run Jobs													
	X001	6	5	1		1								
4/4/56	Long-Run Jobs													
	A123	17	13	4				1					3	
	B456	50	45	5					1	1		2	1	
	Short-Run Jobs													
	Y92	3	2	1									1	
5/4/56	Long-Run Jobs													
	A123	18	16	2									2	
	B456	50	49	1					1					
	Short-Run Jobs													
	Z100	10	3	7		1			3				3	

FIG. 16.—Final Inspection Record Sheet.



Since the accuracy is not of a high order, the method of finding the standard deviation by working back from the range is used.

The average range of the 10 samples obtained from Table XI is 0.02 mm. and for samples of 100, the divisor (derived from Fig. 2) is 5. The standard deviation is therefore :

$$\text{S.D.} = \frac{0.20}{5} = 0.04 \text{ mm.}$$

The standard error of the averages of the samples is

$$\text{S.E.} = \frac{\text{S.D.}}{N} = \frac{0.04}{10} = 0.004 \text{ mm.}$$

The control limits for the mean are :

$$\pm 2 \times \text{S.E.} = \pm 0.008 \text{ mm.}$$

## 6. VISUAL/RADIOLOGICAL INSPECTION

### (a) Factors Involved in Visual Inspection

A rough visual inspection is usually carried out immediately after casting, and a more critical and thorough examination is made before despatch. Unfortunately, each casting produced must be regarded as an individual. This applies particularly to sand castings. It is still true of gravity and pressure die-castings, although as the casting operation becomes more highly mechanized the potential uniformity improves, and therefore sampling methods are not in this case normally applied at the final inspection stage, although they may be applied at the rough inspection stage.

Random defects occurring in castings may be grouped as :

(i) Those associated with the moulding operation, such as bad finish, included sand, misplaced cores.

(ii) Those associated with the pouring, such as flow marks, included oxides, entrapped air, cold shuts or misruns, cracks, and surface shrinkage.

Systematic defects are normally associated with casting techniques or possibly with the design of the casting. Because they are attributable to the same causes as the random defects listed above, there may be some difficulty in recognizing them as systematic. One of the aims of a system of control is to enable this to be done in the shortest possible time.

The approach to the problem of establishing suitable inspection techniques depends on a variety of factors, including the design of the castings, the casting method, alloy, customer's special requirements, or end-use of the components. As already stated, the rough inspection may be carried out on a percentage basis in the case of gravity and pressure die-castings. Usually, faults are corrected at the beginning of a day's production. The critical visual inspection of stressed aircraft components will most certainly be carried out on a 100% basis.

Considerable difficulty may be encountered in attempting to present inspection records in graphical form. A graph could be drawn up, on a date or shift base line, showing percentage defective castings of a particular part number or of castings poured from a particular alloy, but the information gained would be limited. The most satisfactory treatment is to tabulate the information in a methodical manner.

Fig. 16 shows a suggested form of record sheet, in

which the first four columns under the heading "Reasons for Rejection" are associated with the moulding operation and the next five with pouring. It is unlikely to be convenient to use a separate record for each part number or for all castings in one alloy, but grouping long-run jobs and listing them in the same order on successive days, as in Fig. 16, facilitates cross-referencing.

This is not intended to be a complete example, but merely an illustration of the recommended pattern. Treatment of inspection information in the manner just described is elementary and involves nothing more than common sense, but if it serves its purpose in enabling systematic defects to be recognized, and careless moulding and pouring to be corrected, it is unnecessary to elaborate further.

### (b) Factors Involved in Radiological Inspection

Internal defects in castings are attributable to unsoundness or to included air or dross. The unsoundness may take the form of distinct shrinkage cavities in alloys of small freezing range, or dispersed shrinkage porosity in alloys of long freezing range. Alternatively, it may occur as gas porosity resulting from ineffective metal treatment. Entrapped oxide films may result from ineffective metal treatment or may have been introduced by turbulence during pouring. As for visual defects, internal defects will be systematic when associated with a faulty casting technique or faulty casting design, and random when associated with careless metal treatment, moulding, or pouring.

Since radiography is both expensive and time-consuming, it is normally applied only to stressed aircraft castings and because of the conditions of service, no attempt to save time and reduce costs by sampling could be justified.

For long-running jobs in the less highly stressed category, it is possible to obtain some relaxation, not in the number of castings radiographed, but in the number of shots taken of each casting. If it can be demonstrated that a satisfactory casting technique has been established and maintained during the production of at least 10 castings, then the number of shots may be reduced to give sufficient general coverage to detect the presence of random defects. At any suggestion of defects recurring, an immediate return to the full radiographic technique is made and maintained until a further 10 satisfactory castings have been produced consecutively.

## 7. DIMENSIONAL CHECKS

### (a) Factors Involved

Quality-control methods are widely used in the dimensional checking applied to the products of automatic lathes. It might be expected that such methods would find application in foundry work, but the conditions obtaining in the two cases are rather different. In the machine shop, drift due to tool wear constitutes a systematic trend, and the ability of the automatic machine (or the operator) to reset to the same position each time a cut is made will constitute small random variations. Under these conditions either direct measurements or trials with gauges may indicate that a batch is reasonably good, being likely to contain only a small proportion of components outside the limits.

In the sand foundry, however, once the equipment has been made dimensionally correct, drift due to wear is relatively slow and does not normally constitute a serious systematic trend. Variations in critical dimensions result usually from misplacement of cores. In such cases it is common practice to file the core prints to a jig or to use jigs to help in assembling the mould correctly. The potential error is usually large compared with the tolerance allowed on the critical dimension.

In the gravity and pressure die foundry, much closer tolerances can be maintained. Variations may be introduced by a small piece of flash becoming stuck between moving parts of the die and, if this is subsequently dislodged, only a few castings may be affected. More usually, dimensional inconsistencies are introduced by variations in the die coating.

#### (b) *Treatment*

For sand castings it is normally necessary to check critical dimensions on each casting, although in the case of a long-running job an appraisal of the records may suggest that the dimensional checks can be reduced with confidence. It is quite easy to return to full coverage at the first suggestion of trouble.

Dimensional variations are most likely to be introduced in gravity die-castings by the preparation of the die before casting. For this reason, checks are usually made shortly after the beginning of a day's production and any errors corrected before too many unsatisfactory castings have been produced.

If, owing to the manner in which the die operates, the die coating is removed or built up during the course of the day, the most sensible course is to arrange for checks to be carried out when attention is given to the coating rather than at random or regular intervals during the day, just as the product of an automatic lathe must be checked immediately after the tools have been changed.

### 8. SPECIAL TESTS

This category includes such non-destructive methods as pressure testing and fracture and other forms of destructive testing. Pressure testing is not suitable for treatment by sampling methods. Castings are inspected on a 100% basis and defective ones either rejected or reclaimed by any suitable sealing process, depending on the size of the defects and the inspection requirements for the component.

Destructive tests are normally carried out with two objects in view:

- (i) To prove design calculations (e.g. loading tests).
- (ii) To provide information on the manufacturing conditions, not already forthcoming from visual or radiographical inspection methods or from tensile or hardness tests.

Destructive tests involve the rejection of the components tested. Moreover, if the result from the sample submitted is unfavourable, there may not be any practical method of carrying out 100% inspection of the remainder. Correct sampling technique is of the utmost importance in ensuring adequate coverage and, at the same time, economic operation.

A typical example of routine destructive testing is provided by the "machining test" carried out on gravity die-cast motor-car piston castings in LM13-WP

alloy. These are machined on the skirt, the ring belt (to the depth of the ring grooves), and, in certain designs, on the crown. They are finished with a diamond-tipped tool, and the cutting speed and rate of feed are adjusted to give as clean a cut as possible. Under these conditions a mechanical macro-etch is obtained which reveals the presence of minute traces of unsoundness or included matter.

#### (a) *Conventional Treatment*

Castings, selected at random from the day's production, are machined as already described and then inspected visually. A record card is made out, listing the defects and their location, along the lines suggested in Fig. 16. From these particulars, adjustments are made to the casting technique or metal treatment. But this information is of interest only to the founder; the manufacturer is concerned with how many fully machined castings he will be forced to reject because of unsoundness.

#### (b) *Examples of Statistical Methods*

The data provided by the record cards are used for inspection purposes as well as for foundry control. However, it is not readily possible to demonstrate the rather complex principles on which sampling schemes are based by reference to a particular example.

The factors to be considered are:

(i) The number of defective castings expected in batches of a given size. This will be determined by past experience, and in practice may fluctuate between 1 defect in 100 and 1 defect in 5. For this reason the Poisson distribution is used, but by considering batches of size 10 and by varying the expected number of defective castings between 0 and 10, the Binomial distribution may be employed. This simplifies the demonstration of the principles involved without affecting them in any way.

(ii) The proportion of defects in the batches delivered that will be tolerated by the customer. This will be based on past experience with the customer. It is assumed that 1 defective casting per batch will be tolerated, but in practice the proportion of defects tolerated is of the order of 2-5%.

(iii) Sample size. This obviously has a bearing, since the closer the approach to 100% inspection, the more certainly will defective batches be rejected.

(iv) The basis of acceptance or rejection of the sample.

Owing to fluctuations in the manufacturing conditions, the proportion of defective castings varies from batch to batch and, ideally, the sampling scheme should accept all batches containing less than the agreed proportion of defects and reject all batches containing more than the agreed proportion. The object of the following example is to demonstrate how, by varying the sample size and the conditions of acceptance, a reasonable approach to the ideal may be made.

If a batch of 10 castings contain, on the average, 1 defective casting, the chance that a casting picked at random will be satisfactory is  $\frac{9}{10}$ . If a sample of two castings is withdrawn, the probability that they will both be satisfactory is  $\frac{9}{10} \times \frac{9}{10} = \frac{81}{100}$ , which is still high. The chance of picking two defective castings (it



is not to be assumed that, in 100 batches of 10 castings, all the batches contain only 1 defect) is  $\frac{1}{10} \times \frac{1}{10} = \frac{1}{100}$ . The chance of picking a sample containing 1 good and 1 defective casting will be  $2 \times \frac{9}{10} \times \frac{1}{10}$ . In choosing a sample of size 2, the probabilities are given by expanding  $(p + q)^2$ . By converting the fractions to decimals and multiplying by 100, Table XII has been drawn up.

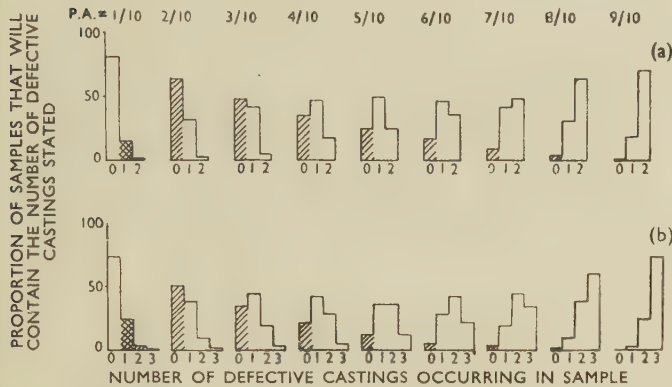


FIG. 17.—Frequency Distributions of Defective Castings Occurring in Samples of (a) 2 Castings, (b) 3 Castings.

P.A. = Process average, i.e. number of defects occurring in batches of 10.

KEY

× × × Unfavourable samples rejecting acceptable batches (producer's risk).  
 /// Favourable samples accepting unacceptable batches (consumer's risk).

Frequency distributions to illustrate the data contained in Table XII are shown in Fig. 17 (a).

TABLE XII.

Average No. of Defects/Batch	Chance of Sample Containing :		
	2 Good Castings, %	1 Good Casting, %	2 Defective Castings, %
1	81	18	1
2	64	32	4
3	49	42	9
4	36	48	16
5	25	50	25
6	16	48	36
7	9	42	49
8	4	32	64
9	1	18	81

TABLE XIII.

Average No. of Defects/Batch	0	1	2	3	4	5	6	7	8	9	10
Proportion of Batches Rejected by Sample, %	0	19	36	51	64	75	84	91	96	99	100

From Table XII, Table XIII has been drawn up to illustrate what happens when a batch is accepted on a defect-free sample, but is rejected when the sample contains 1 or 2 defective castings.

These results are illustrated in Fig. 18 (a), and two points arise :

(a) The founder must agree to the fact that 19% of acceptable batches containing only 1 defective casting will be rejected by unfavourable samples.

(b) The customer will receive a high proportion of batches containing 2 or more defective castings.

The basis of acceptance may be changed and the incidence of 1 defect per sample accepted (because this is agreeable to the customer), but samples containing 2 defects will be rejected. On this basis, Table XIV has been drawn up :

TABLE XIV.

Average No. of Defects/Batch	0	1	2	3	4	5	6	7	8	9	10
Proportion of Batches Rejected by Sample, %	0	1	4	9	16	25	36	49	64	81	100

These results are illustrated in Fig. 18 (b), and it is clear that the system is more satisfactory to the founder, but is now much more unsatisfactory to the customer, because 96% of all batches containing 2 defective castings and 91% of all batches containing 3 defective castings will be accepted by favourable samples.

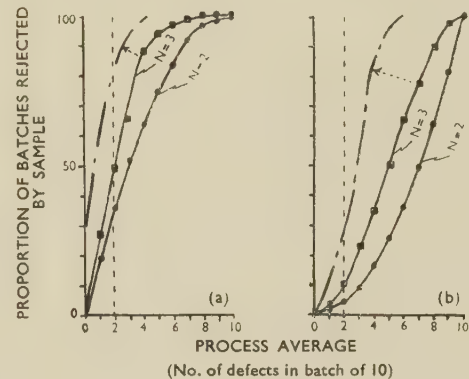


FIG. 18.—(a) Operating Characteristics When Rejecting on Occurrence of 1 or More Defective Castings in Sample. (b) Operating Characteristics When Accepting on Occurrence of 1 Defective Casting in Sample but Rejecting on Occurrence of 2 or More Defects.

TABLE XV.

Average No. of Defects/Batch	Chance of Sample Containing :			
	3 Good Castings, %	1 Defective Casting, %	2 Defective Castings, %	3 Defective Castings, %
1	73	24	3	0
2	51	38	10	1
3	34	44	19	3
4	22	43	29	6
5	12	38	38	12
6	6	29	43	22
7	3	19	44	34
8	1	10	38	51
9	0	3	24	73

The sample size may be increased to 3 and the coefficients of  $(p + q)^3 = p^3 + 3p^2q + 3pq^2 + q^3$  are detailed in Table XV.

Once again the probabilities have been expressed as percentages, although in this case it has been necessary to make some approximations. These frequencies are illustrated in Fig. 17 (b).

As before, two tables may be constructed. Table XVI is based on rejecting the batch when a sample contains 1 defective casting.

TABLE XVI.

Average No. of Defects/ Batch	0	1	2	3	4	5	6	7	8	9	10
Proportion of Batches Re- jected by Sample, %	0	27	49	66	78	88	94	97	99	100	100

These results are illustrated in Fig. 18 (a), and clearly, by increasing the sample size, the system becomes far more stringent.

Table XVII is based on rejection when the sample contains 2 or more defective castings.

TABLE XVII.

Average No. of Defects/ Batch	0	1	2	3	4	5	6	7	8	9	10
Proportion of Batches Re- jected by Sample, %	0	3	11	22	35	50	65	78	89	97	100

These results are illustrated in Fig. 18 (b). Although the discrimination has been reduced, as far as the customer is concerned, a better compromise has been effected, and it is evident that by increasing the sample size still further and by varying the number of defects that cause the sample to be rejected, a balance may be struck. The fairest compromise is achieved when the financial risk taken by the founder that acceptable material will be rejected by an unfavourable sample is equal to the financial risk taken by the customer that batches containing more than the number of defects tolerated will be received.

Practical sampling schemes may be drawn up from the charts given in British Standard Specification No. 2635, although only approximate answers may be found.<sup>4</sup> An introduction to the double sampling schemes of Dodge and Romig and to sequential sampling procedures is given in considerable detail by Moroney.<sup>5</sup>

### (c) Attributes Measured by Assigning an Order of Merit

Although it is possible to measure quantitatively such attributes as grain-size or the porosity contained in a machined section or the surface finish of a component, it is not always practicable to do so. It is often more convenient to place a group of samples in order of merit, that is in order of decreasing grain-size, decreasing porosity, or improvement in surface finish. Numerical values may be assigned to the order of merit. Alternatively, the numerical values may be obtained by a visual comparison of the sample against a standard scale provided by similar samples already placed in order of merit.

This method has the advantage that the numerical values obtained may be regarded as crude measurements of a continuously variable attribute and consequently

may be treated by any of the methods described in the paper. Rating the samples against a standard scale has the advantage that trends due to time are eliminated and results may be compared directly. The effectiveness of one method of grain refinement as against another might be evaluated by means of the *t* test performed on grain-size values, assigned to the samples. Or the reliability of one degassing treatment as against another might be checked by a variance-ratio test carried out on values assigned to sections, machined or polished to reveal porosity.

During the course of initial type tests carried out on a prototype gravity die-cast bracket in LM8-WP alloy, erratic breaking strengths were obtained. At first it was thought that the low results might be attributed directly to the fact that the lugs were unsound, but a cursory examination showed that this was unlikely to be so. To confirm this point, three observers were asked to rate the fractured lugs in order of increasing soundness. The results are listed in Table XVIII, together with the breaking strengths of the components in tons.

TABLE XVIII.—Unsoundness Rating and Breaking Load for Prototype Castings in LM8-WP Alloy.

Casting Ref. No.	Rank Values			Average	Load, tons
	Observer A	Observer B	Observer C		
1	2	3	1.5	2.2	9.6
2	21	16	17	18.0	6.7
3	6	10	11.5	9.2	7.0
4	13	4	8	8.3	10.3
5	7	25	15.5	14.5	8.4
6	5	13	3	7.0	8.5
7	19	26	24.5	23.2	7.3
8	20	20	18	19.3	8.0
9	4	23	28	18.3	9.0
10	1	1	1.5	1.2	10.2
11	10	14	15.5	13.2	7.3
12	25	22	26.5	24.5	7.6
13	17	19	24.5	20.2	7.6
14	12	8	5.5	8.5	10.5
15	24	17	22	21.0	7.4
16	26	27	22	25.0	6.7
17	27	11	19.5	19.2	7.3
18	15	5	11.5	10.5	8.7
19	18	6	11.5	11.8	9.6
20	9	24	11.5	14.8	6.7
21	3	7	11.5	7.2	8.1
22	16	12	5.5	11.2	6.3
23	29	29	29	29.0	9.2
24	14	15	11.5	13.5	7.2
25	11	9	5.5	8.5	6.8
26	22	18	19.5	19.8	10.1
27	8	2	5.5	5.2	9.4
28	23	21	22	22.0	8.3
29	28	28	26.5	27.5	7.6

The numerical values assigned by the 3 observers are compared in Figs. 19 (a), (b), and (c), which demonstrate that their judgement is reliable and that it is in fact possible to assign an order of merit. It is usual in such cases to find good agreement at the extremes and less satisfactory agreement at the centre of the range.

The correlation coefficients have been calculated and are as follows:

Correlation between:

Observers A and B  $r = 0.548$  ( $p = 0.1-0.001$ )

Observers A and C  $r = 0.707$  ( $p = \text{less than } 0.001$ )

Observers B and C  $r = 0.807$  ( $p = \text{less than } 0.001$ )





each of the 1st-order interactions against the revised estimate of the residual, starting with the smallest ( $a/b$ ) and combining the variance with the residual if the ratio is not significant. Clearly none of the effects are large enough to yield a ratio of 4.20 and so, to save unnecessary calculation, they are pooled with the residual as follows:

$$\frac{36.15 + 0.23 + 1.44 + 2.25 + 3.73}{32 + 1 + 1 + 1 + 1} = \frac{43.8}{36} = 1.217.$$

This revised estimate is the basis on which the main effects are tested. These are tested in order of magnitude and, if not significant, they are also pooled with the residual.

However, the ratios for  $a$  (casting technique) and  $b$  (pin material) are highly significant:

$$\frac{a}{\text{residual}} = \frac{13.4}{1.217} = 11.0 \quad (p = 0.01-0.01)$$

$$\frac{b}{\text{residual}} = \frac{28.2}{1.217} = 23.0 \quad (p = \text{less than } 0.001)$$

and, in this case, omitting to pool the sum of squares for  $c$  (which is obviously insignificant) does not affect the size of the ratios nor the level of significance appreciably.

The only significant effects are therefore casting technique and pin material.

The average breaking strength obtained in this experiment was 8.3 tons. The variation in level introduced by the casting technique was:

Original technique	. . .	7.70 tons
Revised technique	. . .	8.90 „

The variation in level introduced by the pin material was:

Mild-steel pin	. . .	7.45 tons
High-tensile pin	. . .	9.15 „

The improvement due to the revised casting technique is quite appreciable, but accounts for only one-half of the variation introduced by the testing conditions. Since the test conditions relate directly to the conditions of service, this information was referred to the designers.

#### ACKNOWLEDGEMENTS

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# METALLURGICAL CONTROL OF QUALITY IN THE PRODUCTION OF ALUMINIUM ALLOY CASTINGS\*

1745

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## SYNOPSIS

The paper reviews some of the more important aluminium casting alloys in common use, and discusses methods adopted and precautions observed in the control of quality in castings made in these and kindred materials, principally from the metallurgical point of view. Certain aspects of control practice, such as those governing dimensional accuracy, are not touched upon, as they fall outside the scope of the paper. Moulding technique also is treated only in broad principle, in so far as it serves to promote metallurgical soundness.

Working procedures and metal treatments are described, together with the steps taken to ensure maintenance of metal quality. Reference is made to methods employed to assess soundness and composition, together with a satisfactory mechanical and metallurgical condition of the product.

## I.—SPECIFICATION MATERIALS

THE first feature to be considered in the manufacture of sand and gravity die-castings in an aluminium foundry is the choice of the right alloy for the component in question. The need for consultation between designer and founder at this stage cannot be too strongly emphasized. It frequently happens that the alloy which seems to offer the best properties on paper may prove to be less suitable from the foundry point of view, relative to the particular application, than others available. A sound casting in an alloy possessing slightly inferior specification properties is to be preferred to a less-sound casting produced in a potentially stronger material, and is usually less troublesome to make. Moreover, it is most important that the alloy agreed upon should conform to one of the recognized specifications which control the chemical composition and mechanical properties.

Aluminium alloys for all casting purposes are now controlled by one or other of two series of material specifications. The first of these, the B.S./D.T.D. specifications, covers material and inspectional details of alloys for aircraft applications; the second, more recent B.S.1490 LM series covers these materials when used in the general engineering field and for all service applications, other than those subject to A.I.D. approval. Indeed, the adoption of the B.S.1490 LM list of approved alloys by service inspectorates and the consequent abandoning of the various individual systems of nomenclature and requirements, represents a considerable simplification and convenience.

The complete coverage of the field of aluminium castings by these approved specifications must necessarily be beneficial, as the use of unsatisfactory materials is rigidly excluded.

## II.—ALLOYS IN GENERAL USE

The modern aluminium casting alloys fall into two main groups:

- (1) Alloys used in the as-cast condition.
- (2) Alloys used in the heat-treated condition.

### 1. ALLOYS USED IN THE AS-CAST CONDITION

The as-cast series comprises alloys of moderate strength suitable for many general engineering purposes and usually possessing good foundry properties. The choice of material is governed by the known characteristics of the alloy in relation to the intended function of the casting to be produced. With this class of material the economic aspect is also important. If the purpose of a component is such that the use of a more expensive high-strength material, with its additional heat-treatment costs, can be avoided, clearly it is policy to do so.

The principal alloy of this type in general use is D.T.D.424A (B.S.1490 LM4), a serviceable material for both sand castings and die-castings. LM4 nominally contains copper 3, silicon 5, manganese 0.4%, with controlled amounts of certain other elements, including magnesium up to 0.15%.

Generally speaking, LM4 is typical of a series of alloys containing significant amounts of copper and relatively large amounts of silicon, this latter element in particular greatly assisting the casting characteristics. Other examples are LM2 and LM24. The former, containing basically 2% copper and 10% silicon, is much used for pressure die-casting and probably accounts for the largest tonnage of this type of light-alloy production in Great Britain today. LM24, with a nominal composition of 3.5% copper and 8.5% silicon, occupies much the same position in American die-casting practice as LM2 does in this country, and is indeed becoming increasingly popular here. These alloys are used extensively for engine components among other products, and are suitable for service at moderately elevated temperatures.

Another important alloy used in the as-cast condition is the binary aluminium-silicon alloy containing about 12% silicon and generally known as Alpax (B.S. 3L33 for aircraft material and LM6 in B.S. 1490). It re-

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quires a chemical treatment of the molten metal to develop its best properties, and when correctly treated is a material of moderate strength and relatively high ductility, having a close, silky fracture. The alloy is exceptional among aluminium alloys in having a very short freezing range owing to the fact that the composition is approximately that of the eutectic; it also has, in consequence, great fluidity when molten and immunity from hot-tearing during solidification. These characteristics make LM6 particularly suitable for castings of intricate shape and section, and also for those required to be pressure-tight.

There are, however, two undesirable features of LM6 alloy in sand-foundry use. The first is a tendency to some degree of gas porosity; this can be aggravated by the chemical treatment referred to above, if the process is not carefully controlled. Under normal conditions, however, experience has shown that slight dispersed porosity has a less deleterious effect on this alloy, in respect of both mechanical properties and pressure-tightness, than it has on other aluminium alloys. The second point is that considerable local cavitation, sometimes of a severe character, may be found in sand castings of this material, a well-known feature resulting from the particular freezing mechanism; this calls for special attention in foundry technique, heavy chilling and generous feeders often being necessary.

Quality control is particularly important with this alloy, both from the point of view of metal condition and that of soundness of the castings. The first is regularly checked by the examination of fractures of sand-cast test-bars and risers from castings. A further guide in this respect is supplied by the tensile strength and elongation values obtained from standard test-bars cast from the melts; these figures are greatly affected by unsatisfactory metal conditions.

X-ray examination of castings to establish and periodically to check foundry technique, together with the daily break-up of castings scrapped for foundry reasons, will ensure a practical control on soundness.

These two classes of alloys, LM4 and LM6, though not fully representative of the as-cast series, account for a considerable proportion of castings produced in this condition.

## 2. ALLOYS USED IN THE HEAT-TREATED CONDITION

In alloys of this class superior mechanical properties are developed by heat-treatment. In the first sub-division are the single-phase solid-solution types, such as the 4.5% copper alloy LM11-W, and the 10.5% magnesium alloy, LM10-W. Both alloys, as heat-treated, are strong, tough materials, well suited for use in highly stressed parts subjected to shock-loading.

Both present rather more difficulty in casting than the alloys mentioned previously. LM11 is somewhat hot-short and has indifferent feeding characteristics which call for particular attention. LM10 also needs special precautions in the sand foundry, because it is particularly prone to absorb gases when molten and during freezing in the mould. This latter feature is largely responsible for the characteristic "mould reaction", which can be detrimental to sand castings in this alloy.

The second sub-division consists of a number of materials containing optimum amounts of alloying ele-

ments, some of which dissolve during solution-treatment to give high strength, while others form high-melting-point compounds which stiffen the matrix and promote retention of strength at elevated temperatures. Some of these alloys are very modern developments designed for the manufacture of components for highly stressed gas-turbine engines, and may contain alloying elements hitherto rare in aluminium practice.

The heat-treated alloys do not, in general, contain an intentional silicon content, and their casting characteristics are usually moderate, being intermediate between those of LM4 or LM6 and those of LM11 or LM10. There are, however, heat-treated alloys of high silicon content with additional elements for special uses, an example being LM9-WP, often described as Alpac Gamma, a hard, strong material used where these properties are required in combination with the corrosion-resistant and casting properties of Alpac (LM6).

LM8 alloy, containing 5% silicon with 0.5% magnesium, possesses excellent foundry properties and produces, in the heat-treated condition, material which is growing increasingly popular for the manufacture of cylinder heads and other castings required to have an exceptional degree of pressure-tightness.

In the die-casting field, the principal heat-treatable alloy is LM22-W, containing copper 3, silicon 5, and manganese 0.4%. As the basic composition indicates, LM22-W is an adaptation of the general-purpose alloy LM4, but it is based on high-purity materials, incidental elements being controlled within narrow limits. By virtue of the specially designed composition, die-castings in LM22, when suitably heat-treated, are strong, tough components of uniformly high metallurgical quality, practically free from latent age-hardening tendencies. This alloy, indeed, compares quite favourably in mechanical values with the older-established high-strength alloys and has the advantage of much better foundry properties. The improvement in casting behaviour as compared with LM11, for example, is again largely due to the silicon content of LM22.

A review of aluminium casting alloys in present-day use would not be really representative without some mention of the alloy usually known as R.R.50 (L51 and LM23-P). This is suitable for sand- and die-castings, and has a nominal composition of copper 1, magnesium 0.1, silicon 2.5, iron 1, nickel 1, and titanium 0.15%.

LM23-P is an excellent foundry alloy, its principal feature being that castings of adequate strength for many general purposes can be produced by a simple heat-treatment at 155°–170° C. This property permits the manufacture of large and complicated castings free from the risk of distortion which might occur in such cases if material requiring solution-treatment at high temperature followed by quenching, was employed.

In the aircraft industry during the war, and in many other applications of more recent times, very large tonnages of this alloy have been used.

## III.—CONTROL OF COMPOSITION

In a foundry where many different alloys may be in regular use at the same time, a dependable system of alloy segregation is essential for adequate control, and



the greatest attention to detail at vulnerable points must be encouraged in every way.

While the effects of very slight contamination with foreign materials or by accidental admixture of alloys may be less serious with some of the general-purpose casting alloys, they are likely to be disastrous with high-tensile-type materials; even the former can tolerate very little contamination by certain elements. For example, iron pick-up resulting from careless working with badly coated pots or furnace tools, causes serious embrittlement in LM4 alloy. Contamination of the same alloy with quite small amounts of an aluminium-magnesium alloy produces similar effects, and yields metal which will not only be brittle when cast, but which develops still further brittleness on natural ageing. In the case of LM6, contamination with magnesium impairs the ductility also, introducing the age-hardening intermetallic  $Mg_2Si$ , while contamination with copper not only reduces the corrosion-resisting properties, but also interferes with the requisite chemical treatment and thus reduces the toughness of the cast alloy. Iron, too, is detrimental, producing brittle intermetallic compounds, with consequent loss of ductility.

The high-strength heat-treated alloys LM10 and 11, previously quoted, are particularly sensitive to contamination. These materials are made from aluminium of purity higher than 99.7% in order to limit the contents of iron and silicon—the two impurities normally present in aluminium ingot—to a safe tolerance. Increase in the content of either or both of these elements entails a progressive deterioration in strength, ductility, and toughness.

These specific instances are cited as examples of some of the dangers of contamination from the material point of view. The economic aspect of contamination is also extremely serious, for apart from the loss of time, fuel, and labour, should castings be made in faulty material, the depreciated value of contaminated metal is self-evident. There is no question but that the expense in time and labour required to ensure the best possible material identification and segregation at all stages is entirely justified.

#### IV.—MATERIAL CONTROL

In practice, material control is effected on the following lines:

The details of the job and the material required are clearly marked on the moulder's card and are checked by a technical assistant who has a copy of the planner's list. Precise details are given in making out requisitions to the metal stores for ingot material and a signed tally, repeating the weight and alloy details, is returned from the stores together with the metal ordered to the melting station making the request. This receipt is checked by the furnace staff, who are also encouraged to check the ingot maker's stamp on the materials received.

At the other end of the system, from which the second component of any melt, i.e. current process scrap, is derived, great care is also taken to ensure the despatch of the correct material to the furnaces.

At the knock-out station, runners and risers are identified at the earliest possible moment by marking with a

fast-drying paint—a rigid colour identification scheme is used—before stripping down has proceeded very far. Meticulous care is taken throughout, both at the first viewing station and particularly at the site where sawn-off scrap is returned to the furnaces.

The transferred scrap is received at the furnace sites and stored in clearly marked bins, which are in open view and are constantly supervised by the control staff when fresh material is brought down from the dressing shops.

An extension of these precautions is carried out in the refinery, where scrap of a lighter nature, such as gullies, &c., together with material not considered suitable for direct re-issue on production melts, is remelted, refined, and cast into ingots. The greatest care is taken to ensure that the furnace charge is of the correct material, and each melt is tested analytically and examined for cleanliness and general condition before re-issue to the foundries.

In the control of input to the furnaces in the foundry other important matters require attention, such as examination of scrap castings before return to see that these are free from adhering chills, concealed core-wires, &c., and also that the metal is clear of baked-on sand. Shot blasting is frequently employed to clean up scrap affected in this way.

Control of composition, apart from the considerations mentioned, is naturally dependent on the provision of representative samples from production melts. For this purpose, test specimens are cast in an iron book-type die, giving a sample some 6 in. high, 2 in. wide, and  $\frac{5}{16}$  in. in thickness.

These specimens solidify very quickly, so that segregation effects across the length and width of the piece are virtually negligible. Some slight segregation through the thickness is assumed to exist, and in sampling for chemical analysis by drilling the complete thickness is used in preparing the sample. In the case of samples for spectrographic purposes, a measured length of the lower part of the specimen is always employed, and this is milled down to a measured thickness proved by experience to be most suitable; this is, of course, done from the same face on every occasion. In this connection, too, it is most important that the melt should be stirred with a light upward motion, just before a sample is taken, to disperse segregation effects within the melt, for the most meticulous analytical work is clearly quite abortive if the sample is unhomogeneous or not fully representative.

By using approved and certified materials in the foundry, and by employing reliable workmen and exercising good supervision, it is possible to reduce considerably the amount of analytical work required. Under these conditions, the A.I.D. accepts a minimum of 5% of melts to be fully tested per alloy, per department, per working shift, although a higher percentage is the more usual practice. Spectrographic methods permit the checking of a larger number of samples, particularly for contents of minor alloying elements and impurities, and in general, the spectrograph has proved a most valuable analytical tool.

When sampling, the test specimens should be taken as near to the time of casting as possible and after all metal treatment is completed, so that there can be no question about the authenticity of their representation. This applies also to the bars cast for mechanical-test purposes. In this latter case, a set of three bars is cast to represent

every inspectional melt, and a reduced proportion, usually 1 in 5, where the application is commercial only.

For all alloys, with one exception, the standard test-piece for sand-cast work is a test-bar of about 7 in. effective length and 1 in. dia., surmounted by an integral feeder head, there being no separate runner/riser system.

The exception is the 10.5% magnesium alloy, LM10, where the approved E-type test-piece is used, consisting of four shaped bars run from a common runner and adequately risered. The pattern design is mandatory and is shown in the specification.

## V.—CONTROL OF MELTING PRACTICE

### 1. MELTING POTS : PREPARATION AND MAINTENANCE

Aluminium casting alloys are commonly melted in steel or refractory crucibles, and the first point bearing on the control of quality which requires attention in this operation is the procedure adopted to avoid contamination with iron when steel is used.

The choice of melting-pot material depends on the nature of the alloy and whether the molten metal is to be contained for a comparatively short time, as in the preparation of most sand-foundry melts, or to be held for fairly prolonged periods such as may occur in a die-casting foundry.

In general, alloys of high silicon or magnesium content are unsuited for use in steel pots, however good the protective coating applied. Such alloys, which include LM1,2,5,6,9,10,13, and 20, should be melted in refractory (usually plumbago basins). LM11, although it contains neither silicon nor magnesium in significant amounts, is also best melted in plumbago to avoid even the slightest chance of iron pick-up, for the reasons given.

Although certain other alloys for sand-foundry work, such as LM8, 14, and 23, contain magnesium and silicon, these elements are present in rather smaller amounts, and steel crucibles have proved quite satisfactory in practice, provided that the number of consecutive melts between re-coatings is strictly limited to a proved degree of safety, usually two such melts. It is advisable, and usually more convenient, to use steel melting pots wherever possible, because they have better thermal properties and, owing to their non-porous nature, there is less likelihood of gas pick-up.

To ensure adequate maintenance of pots, it is well worth while to set up a small specialized department, whose duties are the scraping down, cleaning, and recoating of this equipment. Protective washes are usually made from one of the aluminous or magnesia proprietary coatings easily obtainable and mixed with a sodium silicate solution to act as a binder. Ladles, skimmers, and all furnacemen's tools are cleaned daily and treated with this preparation.

The coating of plumbago pots is not generally considered essential, but a suitable wash helps to minimize gas absorption and assists in prolonging the life of the crucible, particularly when corrosive fluxes are used, as in the case of LM6 and LM10. With LM10, also, the coating should be as chemically inert as possible, to prevent silicon contamination which might otherwise result

from reaction between silica and the magnesium of the alloy.

In the case of melts in the die foundry, the use of plumbago crucibles is always advisable, whatever the alloy, owing to the frequently prolonged periods for which molten metal is held.

### 2. METAL TREATMENT : DEGASSING

The second point in dealing with melting practice, and one of great importance in the control of metal quality, is gas absorption and the removal of gas from a melt before casting. Molten aluminium is capable of dissolving considerable quantities, and the effect of such dissolved gas, if it is not removed, is to reduce the mechanical properties, pressure-tightness, and general condition. The effect of the partial escape of gas during the solidification of gassy metal in a sand mould is shown in the characteristic "pin-holing" to be seen on machined faces of castings affected in this way. The appearance is unsightly and unsatisfactory.

Gas absorption (the gas being almost entirely hydrogen derived from moisture and hydrocarbon decomposition) can arise from several sources :

(i) The use of metal which has been badly stored and which has accumulated surface-corrosion products. Naturally, every precaution should be taken against this possibility.

(ii) Pick-up from flame and combustion gases impinging on the metal surface. This is prevented by using an inert cover flux, many proprietary types of which for use with aluminium alloys are available, and the strict avoidance of forced melting or free flame in contact with the metal charge, particularly when molten.

(iii) Pick-up from melting pots and tools which have not been sufficiently well preheated to destroy every trace of moisture or hydrated material. The adequate preheating of freshly coated steel pots before recharging is of particular importance.

Assuming proper attention is given to these details, which should be quite easy in routine practice, aluminium alloy melts are usually of very low gas content. Nevertheless, it is now general practice to apply a degassing treatment to all molten metal used for sand-cast work.

For this purpose the metal is raised to 700°–720° C., under its protective flux layer, heating is reduced, and the melt is stirred with a circular movement to effect a separation of the spent flux, which is skimmed off as a dry, powdery mass, leaving a clean metal surface. Degassing is effected by plunging into the molten alloy some  $\frac{1}{8}$ – $\frac{1}{4}$  wt.-% of a proprietary compound based on hexachlorethane, which is usually in tablet form for convenience. The additions are made in portions of one-quarter of the total treatment at a time, so that the effect is regular and controlled. The principle of the treatment is that the degassing compound decomposes in the molten alloy, liberating mainly aluminium chloride vapour, which sweeps out any previously dissolved gas and is itself practically insoluble in molten aluminium.

To ensure that the metal prepared for any sand casting of importance has a sufficiently low gas content, the melt is tested before casting, by the B.N.F. reduced-pressure test method. A sample of the metal is baled out into a small iron crucible which has previously been heated and "washed" in the melt, and is then transferred to a



small autoclave in which the test sample is allowed to solidify under a reduced pressure of some 40–20 mm. mercury. A heat-proof glass window in the lid of the autoclave allows visual inspection of the freezing sample; unduly high gas contents are immediately evident from the appearance of a swollen, convex surface, caused by the upward pressure of the dissolved gas. Lesser degrees of gassing will show small protuberances, while a really satisfactory sample will show a flat or even concave surface. With a little experience, gas control by this means is both simple and effective. Figs. 1 (a)–(c) (Plate XLI) show the progress of the degassing operation in alloy LM14.

In the author's experience, it is unwise to assume that, because an apparently effective melting and degassing treatment has been observed, all melts so treated will automatically follow the same pattern and render gas-testing unnecessary. Gas pick-up can be so insidious that this simple and essentially practical test should be applied to all important melts.

### 3. GRAIN REFINEMENT

The holding of molten aluminium alloys for considerable periods, especially at elevated temperatures, may harm their casting characteristics and impair the physical properties of the product by causing grain coarsening. In modern practice, therefore, it is usual just before degassing to treat sand-foundry melts with one of the various grain refiners marketed, as much as  $\frac{1}{2}$  wt.-% being used in some cases. Figs. 2 (a) and (b) (Plate XLI) illustrate coarse grain-size in a sand-cast LM4 test-bar and a similar specimen from the same melt after grain refinement.

Cibula\* has shown that grain refinement by such means involves the formation of very small particles of certain compounds, notably carbides or borides, which act as nuclei of crystallization for the aluminium-rich primary crystals. Titanium boride appears to be particularly effective, and the essential elements are usually introduced in the grain-refining preparation as double fluorides of an alkali metal. The preferred grain diameter varies with different alloys, but is usually in the range 0.05–0.03 cm., and if undue coarseness is noted in any particular case, special regard is paid to such a batch of castings, especially from the point of view of ensuring representative mechanical properties and of pressure-tightness, if applicable.

After grain refining and the subsequent degassing treatment, the metal should be used as soon as possible and, in the case of an unexpected delay on the moulder's part, the molten metal should be kept at a low temperature and not brought up for treatment at all until the position is clear for progress.

### 4. TEMPERATURE CONTROL

While some degree of superheating of the melt above the desired casting temperature is obviously necessary to allow for transfer loss, especially in cases where metal has to be baled into casting crucibles, and not cast direct

from the melting pot, it should be as small as possible. The use of unduly high temperatures promotes gas absorption and grain growth, particularly if the time is prolonged. The maximum melt temperature is rarely as high as 800° C. and is generally 50°–60° C. lower than this. In the case of LM10 and 11, the maximum permitted is 720° C., because these alloys are particularly sensitive to overheating.

Accurate pyrometric control is essential and, apart from portable instruments which may be moved to any desired casting site, fixed instruments with multi-point switching may be used to cover every section of the sand foundry. The instruments should be verified by the pyrometry maintenance staff, who normally check daily 20% of the instruments in regular use against a potentiometer. In this way, every instrument is checked at least once weekly, and the portable instruments used for the casting temperatures themselves are checked daily.

The casting temperature employed in any given instance is the lowest which will satisfactorily run the casting and give, in practice, a reasonably uniform system of temperature gradation, so that any tendency to drawing at bosses and large changes of section is minimized. If the metal is too hot, this factor may lead to marked segregation and tearing effects. Only experience and trial, having due regard to the size of mould and the alloy used, can indicate the optimum conditions.

### 5. PRECAUTIONS WITH PARTICULAR ALLOYS

#### (a) LM6

Two of the alloy series require special attention. The first is the aluminium–silicon alloy LM6. This is unique in that the mechanical properties required in the product depend, as previously mentioned, on a special refinement of the microstructure. This refinement is achieved by “modification”, which is effected by the addition of sodium to the melt, the sodium being introduced either in the metallic form or by treating the melt with a salt mixture, comprising sodium fluoride and chloride, which produces sodium by interaction with the molten metal. The effect of the sodium addition is to suppress the normal crystallization of the aluminium–silicon eutectic and in this way to produce a marked reduction in the particle size of the silicon in the cast structure. The resultant metal is tough and ductile.

In practice, the molten alloy is usually first treated with a hexachlorethane tablet, not only to degas, but also to destroy the “residual modification” arising from the use of “modified” ingot or process scrap. The predetermined amount of sodium (or salt mixture, thoroughly dried) is then applied. The “salts method” of preparation gives melts freer from gas and is generally preferred in the sand foundry, as ordinary commercial sodium contains much gas and is usually contaminated with hydroxide, which is also likely to introduce hydrogen.

However, two recent developments may improve this position. The first consists of the introduction of a capsule containing sodium and a degassing agent combined, a procedure which seems unorthodox in theory but is said

\* A. Cibula, *J. Inst. Metals*, 1949–50, 76, 321.

to be effective in practice. The second is the commercial preparation and use of vacuum-melted sodium, which is virtually gas-free. Both these developments reflect considerable credit on their originators. The use of these sources of metallic sodium for the modification of sand-foundry melts may become more popular because sodium is easier to use than the salts method, a less-critical working temperature may be used, and the erosive action on the plumbago melting pot is negligible as compared with that produced by salts.

The amount of metallic sodium usually required is some 0.05–0.10 wt.-%, and this is introduced by plunging, using a suitable holding tool. After 5 min. or so has been allowed for the melt to clarify, casting is carried out within a further 15 min., the effect of modification in the molten metal being only temporary.

When the salts modification process is used, the temperature must be accurately regulated to that known to give the most consistent results; this is usually 760° C. The time for which the mixture is left in contact with the molten alloy, i.e. actual processing time and standing time, is also kept uniform.

The control of correct processing is assessed by fracture tests and mechanical-testing results, and becomes in practice a routine operation. If the general trend of silicon alloy melts appears to be departing from the accepted standard—this may sometimes arise in a change of supplier's ingot—microscopic examination is resorted to, in order to study the situation more closely. Fig. 3 (a) (Plate XLI) shows a fracture in a sand-cast test-bar of unmodified LM6 and Fig 3 (b) the corresponding coarse microstructure. The effects of modification by the salts method are illustrated in Figs. 4 (a) and (b) (Plate XLI).

In die-casting practice, the heavy chill effect imparted by the metal dies is often sufficient to give a good, close structure without the use of sodium, when the castings are of thin section. For castings of heavy section, sodium is used, but in considerably smaller amount than for sand-cast work. In this respect, die-casting practice is less critical, the presence of small amounts of gas in the melt being more tolerable than with sand casting.

#### (b) LM10

The second alloy requiring special treatment in the sand foundry is the aluminium–10.5% magnesium alloy L53 or LM10. In the first place, the use of the normal protective fluxes suitable for the bulk of aluminium alloys is excluded, because they are based on sodium silicofluoride mixtures; this renders them not merely inefficient for use with LM10 but definitely detrimental, as this alloy is harmed by sodium contamination. A proprietary flux based on magnesium chloride is used, and as such mixtures are deliquescent, the preparation is normally fused by the manufacturers and supplied in this condition. The need for keeping fluxes for foundry use in dry condition is particularly important in this case.

The flux is liquid at the metal temperature, 680° C., and after serving its purpose as a cover flux during melting, the heavy flux layer (some 3% is normally used) is well "washed" into contact with the molten metal to clean up dross. LM10 is not readily degassed and usually requires 0.5% of degassing tablets added in small regular increments. The reduced-pressure test for gas content is of particular value in this case.

## VI.—CASTING PRACTICE

It is not the purpose of this paper to discuss casting practice in any great detail, but certain general principles are mentioned to call attention to features which must be closely controlled if uniform quality in the product is to be ensured.

### 1. GATING

Aluminium alloys in the molten state tend to give rise to a scummy oxide which is liable to be trapped in the melt, if care is not taken. The metal should, therefore, be as tranquil as possible, both during pouring into the mould and also in the mould itself; this end is achieved by means of suitably designed running systems. Bottom running, with numerous ingates of small section, is generally to be preferred to more direct method of entry. The use of strainer grids in pouring bushes and main gullies, to restrain scum and control flow, is routine practice, especially with larger castings. Freer running conditions are necessary for alloys containing considerable amounts of magnesium, as these tend to be more sluggish in flow.

Except for those cases where only a few castings are required off a pattern, the running and feeding systems are incorporated in the pattern equipment to ensure reproducible results.

### 2. FEEDING

The feeding characteristics of aluminium alloys vary considerably, those having a substantial silicon content being usually superior to those without. Unfortunately, from this point of view, many of the modern high-strength alloys required for important castings are not primarily silicon-containing and have indifferent feeding characteristics. This deficiency has to be met by the extensive use of chills and massive feeding heads.

The size and positioning of chills can be determined only by trial and error and by the light of experience; thickness of section, degree of feed available, and position in relation to adjoining thinner areas are the main considerations. Tears may result from stresses set up by injudicious chilling, so that when a suitable balance of chills and feeders has been found the pattern equipment should ensure that the chills are always accurately located. Probably few major castings are made nowadays that are not very heavily chilled in the more vital areas. LM10 is a particular case in point, where heavy chills and large feeders are usually required to obtain consistently sound castings.

The ideal aimed at is metal of the right temperature and chills and feeders so disposed that no part of the casting solidifies prematurely in relation to the other parts, thus ensuring that thermal stresses liable to cause hot-tearing are reduced to a minimum, and yet so arranged that the casting as a whole freezes before the feeder head. The use of exothermic compounds or foam-plaster insulating sleeves—both designed to keep feed metal molten for longer periods—is increasing in practice.

It is a general feature of quality control that, in the case of important castings or where long runs of a job are expected, prototypes are most thoroughly inspected and tested before continuing production. Break-up tests, where practicable, are of assistance, the appearance of



fractures and of machined sections, particularly in regard to grain-size distribution, being a good guide to general soundness, especially if supported by X-ray examination. When a foundry technique has yielded a fully tested and satisfactory casting, a comprehensive and detailed record is made the basis of production control. Such a record is filed for future reference and also to assist in the development of techniques for castings of similar type.

### 3. MOULD REACTION

Another feature of casting practice which has an important bearing on the production of sound castings in alloys containing much magnesium, such as LM5, LM10, and LM14, is the means taken to obviate the characteristic gas absorption (mould reaction) which such alloys exhibit when cast in sand moulds. This subject has been dealt with at length by the British Non-Ferrous Metals Research Association. It is sufficient here to say that the supervision and maintenance of the special sand additives, ammonium bifluoride, &c., used to inhibit sand reaction, and the replenishment in this way of used sand, is important in the control of the many castings made in these alloys. Supervision of these features is a function of the sand-testing laboratory in the foundry.

The use of fractional amounts of beryllium in melts of these alloys is again a very helpful factor in the inhibition of mould reaction.

## VII.—HANDLING AND IDENTIFICATION

Reference has previously been made to the method of colour identification of alloys at the knock-out stage for purposes of material segregation. It is equally important, when the casting is sufficiently exposed, for it to be stamped clearly with details of alloy, cast date, and reference, so that its production history is known.

A further point at this stage is to exercise reasonable care in the knock-out and cleaning operations. Some aluminium alloys are prone to be easily damaged by rough handling while hot; sand-cast LM10 in particular is liable to damage and needs special care, for although it is a tough, strong alloy when heat-treated, it is rather brittle and likely to crack easily in the as-cast state.

## VIII.—HEAT-TREATMENT

It is probably true to say that heat-treated castings represent the major part of the output of a modern aluminium casting foundry, and that practically all large and important castings are heat-treated.

Heat-treatment of aluminium alloys normally consists of a solution-treatment, more often than not followed by a low-temperature precipitation-treatment. Primarily, solution-treatment consists of holding the castings at a temperature just safely below the solidus for a sufficient length of time for the essential intermetallics present in the cast state to be taken into solution by diffusion; the castings are then rapidly removed from the furnace and quenched in a suitable medium. A number of variables require close control to ensure uniform quality of the finished article:

(a) The temperature must be strictly in accordance

with the requirements of the specific alloy; temperatures too low will be less than fully effective, and those too high will result in spoilt castings owing to sagging or blistering caused by local liquation of eutectic. As an example, LM11, the binary aluminium-copper alloy, requires solution-treatment at 530°–540° C., and in view of the fact that the eutectic starts to melt at 548° C., it will be seen how precise temperature control must be.

(b) Time of treatment is dependent on physical condition, thickness of section, grain-size, whether sand or chill cast, and so on. The time for solution-treatment may vary, therefore, from 4 to 24 hr.

(c) The quenching medium is frequently hot or boiling water held in a tank large enough to make the operation practicable. For sand castings of a complicated nature, involving very considerable changes of section, the quench medium is oil, held at about 80° C., and used in sufficient bulk to enable a full load to be quenched without a rise in temperature at equilibrium of more than 40° C., to avoid any incipient ageing effects and to reduce fire risks.

To ensure the required accuracy of temperature control, electric resistance furnaces with powerful air circulation are used, and these are fitted with sufficient thermocouple points to provide readings at the top, middle, and bottom zones. Potentiometric or electronic controllers are standard equipment, together with an alarm mechanism to advise immediately in the case of overshoot. These instruments are supervised daily by the pyrometry maintenance staff and are checked against a standard potentiometer at least once a week. Once a month the whole of the pyrometric units are checked by the insertion of a separate thermocouple into the furnace connected to a potentiometer, so that an independent check can be made between a master outfit and the production equipment. Accuracy of control must be at least as good as  $\frac{1}{2}\%$  of the scale reading and is usually well within 1° C. at the working temperature.

Procedure in loading charges for solution-treatment is important. Castings are carefully located on rigid perforated trays, due regard being paid to the need for free air circulation. Heavy castings are mounted in such a way as to minimize any possibility of distortion due to sagging, e.g. overhanging sections are suitably supported with packing pieces.

After solution-treatment and quenching, which should be carried out with a minimum of delay after removing the load from the furnace, the charged assembly is left in the quench medium for sufficient time to permit temperature equilibrium between the charge and the liquid to be established. The load is then withdrawn and the castings are drained, oil-quenched work being degreased.

Some alloys, such as LM10-W and LM11-W, are intended for service in the solution-treated condition, but the majority of castings are given a subsequent precipitation-treatment to produce maximum strength and hardness, though with some loss of ductility. This second or precipitation-treatment is usually carried out at temperatures varying from 160° to 215° C., depending on the alloy, and is conveniently done in gas-fired stoves, closely controlled by thermostatic devices. Stoves in which the combustion unit is well-insulated from the process chamber, the latter being heated by forced hot-air circulation, are very effective. As in the case of electric furnaces, accurate recording and control instruments are

fitted. After the precipitation-treatment, the castings are withdrawn and allowed to cool in air.

All charge details should be recorded as to weight, date, and description, the relevant test-pieces being heat-treated with the load and tested to confirm efficiency of treatment. Records should be detailed and fully comprehensive and, under most official inspections, must be held available for a period of 5 years. All pyrometric check details are recorded and preserved in the same way.

## IX.—INSPECTION

Visual inspection is usually two-fold. At first view, with the castings freed from runners and risers (obvious scrap, such as mis-runs and the like, are picked out before the sawing operation), the work is quickly but thoroughly inspected for faults, and at this stage such occasional repair work as is deemed necessary is decided upon. These operations entail approved methods of welding for the most part.

After dressing, castings are heat-treated, if specified, and stamped with a suitable symbol to show that heat-treatment has been carried out. After other tests designed to ensure that dimensional details are satisfactory, all castings are again critically viewed and, in certain cases, crack-detection methods are applied.

Of these, the best known is the "chalk-and-oil" test. This consists of immersing the clean casting in a bath containing 20 parts lard oil and 80 parts paraffin at 90° C. The casting is left immersed for 15 min. or until the bath regains temperature, after which it is withdrawn and rapidly dried off in clean wood sawdust. The excess sawdust is then thoroughly removed—an important point—and an even film of fine French chalk is blown over the entire surface of the casting, using a suitable insufflator. The casting is then allowed to cool to room temperature and to stand for a time.

The principle involved is that the penetrating oil mixture will enter every crevice when the casting is hot; on cooling, the excess oil tends to be forced out of the fissures by contraction or by surface-tension effects, leaving evident traces on the white powdered surface.

Other methods of crack detection are now available and consist, in general, of treating the scrupulously clean casting with a penetrant dye solution, either by dipping, swabbing, or spraying, and allowing a period of 10 min. or so for absorption to become complete, after which the excess dye is thoroughly washed off.

A developing fluid is then applied in such a manner as to give a thin even coating. After the casting has dried off and stood for a time, cracks are revealed as coloured lines on the white background provided by the developer.

In some applications the penetrating liquid contains a fluorescent chemical and the final inspection is made by ultra-violet light in a darkened booth. Cracks show up as glowing lines on a dark background.

Many castings are also required to be pressure-tested, and this is done by sealing all apertures but one with heavy rubber pads under mechanical pressure, and joining a source of compressed air to the one open aperture. The whole rig is then immersed in a suitable liquid—usually warm water—and the specified pressure of air applied; porosity is indicated by the escape of air bubbles. Leaking castings which show very moderate porosity may

be reclaimed, with the customer's consent, by using the baked-linseed-oil method. This method is not applicable when the finished casting is required for use in contact with ethylene glycol or any other grease solvent; in such cases, one of the modern plastic compounds is used.

The first method of impregnation, outlined in A.I.D. Instruction D401, briefly consists of placing the clean, warm castings in a pressure vessel and exhausting the air in the chamber until a fairly high degree of vacuum is reached; this is normally about one-sixth of an atmosphere. Boiled linseed oil is then admitted, and a pressure of some 90 lb./in.<sup>2</sup> is maintained, the assembly being left in this condition for 20–40 min. On removal the castings are allowed to drain, excess oil being removed by air blowing. To complete the process, the work is baked at 160° C., for some hours to polymerize the oil; excess oil after baking is removed by washing and brushing. All castings treated in this manner are again pressure-tested before despatch.

Other quality-control checks, such as break-up for examination of fracture, uniformity of dimension, and examination of macro- and microstructure, have been previously referred to; these tests would be carried out extensively on prototypes and in the earlier production stages, but the frequency of testing is naturally much reduced when a generally satisfactory production standard has been arrived at.

As regards internal soundness, X-ray examination is of the greatest value in assessing the quality of any light-alloy casting, the low specific gravity of these materials making them particularly suited to this method. X-ray sets of moderate power, say 200 kV., give films of excellent density and definition. The type of radiation from sets of this calibre has considerable latitude and can accommodate, in the same shot, fairly substantial section changes. The harder radiations emanating from radioactive isotopes have been found to give indifferent results with light alloys. The only one of the series so far known to give a suitable emission is thulium<sup>170</sup>, and unfortunately the sources at present available are of insufficient power for radiographic work; exposure times would be so lengthy as to render the method quite impracticable.

The drawback to X-ray examination is its high cost, but nevertheless, because of its value as a means of inspection, radiography of light alloys is rapidly growing in practice. In the case of light-alloy components intended for aircraft use, the efficacy of X-ray examination is so highly regarded that most important functional castings are inspected by this means, many of the more highly stressed components being examined by officially approved techniques, which must be rigidly adhered to.

X-ray examination of commercial castings also is now common at the prototype stage, with periodic checks during the production run. The effect of any significant change in foundry technique is usually checked by X-ray examination.

In planning his method of examination, the radiologist takes into account those basic features of manufacture which suggest, from practical and theoretical considerations, where faults are most likely to occur. Such details include the design of the casting, with particular reference to section change, the method of moulding, and the material used. The X-ray technique must be adequate to explore every salient part of the casting.

The radiologist notes the character and frequency of



defects observed and, from experience, is able to assess their relative importance and, in consultation with the production and technical personnel, to correlate the occurrence of these faults with unsatisfactory features of moulding or casting techniques. In this way X-rays serve to promote the production of sound castings, and assist the inspection department in its duty of assessing the quality of the finished work.

Some of the results of X-ray examination in revealing the existence of fissures, porosity, and blowholes are shown in Figs. 5 (*a*), 6 (*a*), and 7 (*a*) (Plate XLII), while measures to correct these defects are illustrated in Figs. 5 (*b*), 6 (*b*), and 7 (*b*).

The final item to be mentioned is the routine checking carried out by the chemical and mechanical-testing departments, both of which work to a methodical and comprehensive schedule of testing on the lines already

indicated. In many instances, the test details produced in these departments are necessary to the Inspection Authorities, for the purposes of certification and formal release of castings.

The primary purpose, however, of these laboratories, is to confirm the efficacy of the procedures previously outlined for the control of quality of the firm's products, and to record those trends which it is the function of the technical departments to control and regulate, for the maintenance of the highest practicable standard of production.

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# 1746 THE CONTROL OF QUALITY OF MAGNESIUM-BASE ALLOY CASTINGS\*

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## SYNOPSIS

Practical steps which contribute to high quality in sand castings are considered, and an account is given of inspection techniques designed to show whether high quality has in fact been achieved. Methods are described for examining the various possible defects so as to determine their nature and origin, and to indicate the appropriate remedy. Special points relating to gravity die-castings or arising from the effects of thermal or protective treatments are mentioned. Brief consideration is given to the practical significance of various defects. Finally, some observations are offered concerning production arrangements which it is thought can facilitate the attainment of high quality.

## I.—INTRODUCTION

THE paper embraces sand castings and gravity die-castings,§ and deals with three aspects of the control of metallurgical quality, namely, practical steps directed to the attainment of high quality, routine inspection of the castings obtained, and determination of the origin of defects so that remedial action can be taken. Only a few of the possible defects are here illustrated, for in the majority of cases it has been possible to cite satisfactory illustrations from existing publications.

Ideally, a casting should be correct in composition, free from inclusions, porosity, segregation, folds, cracks, blowholes, and surface blemishes of all types. In addition, it should be correct dimensionally, of suitable grain-size, and free from internal stress. Heat-treatment to develop satisfactory mechanical properties and subsequent protective treatments may also be required.

The general principles of melting and casting magnesium alloys are well known,<sup>1,2</sup> and Wilkinson and Hirst<sup>3</sup> have recently described suitable procedures for use in the production of billet and slab for working. In the present paper, therefore, no detailed account of melting and fluxing techniques is given, but attention is directed to such practical points as are known to affect casting quality.

Magnesium alloys raise problems of special interest in the casting field because of their high chemical reactivity, low density, low volume heat capacity, general fine grain-size, and tendency in some cases to exhibit microporosity. Many of these are not simply foundry problems, so that it becomes necessary to consider the control of such aspects of founding as influence the metallurgical quality of the castings.

## II.—MAGNESIUM CASTING ALLOYS

The alloys fall roughly into two groups, characterized by the presence of either zirconium or aluminium. Alloys containing zirconium now constitute the major proportion of magnesium castings for aircraft usage in Great Britain.

### 1. ALLOYS CONTAINING ZIRCONIUM

Although the liquid solubility of zirconium in magnesium alloys does not exceed 0.6–0.8%, its presence exerts a strong grain-refining effect in castings.|| Zirconium is readily precipitated from solution in the molten alloy by aluminium, silicon, iron, manganese, carbon, hydrogen, and certain other elements.¶ Only the zirconium dissolved in the liquid alloy at the time of pouring is effective in refining the grain and improving the mechanical properties. Because of pick-up of impurities from fluxes, crucible materials, &c., it is necessary to add an excess of zirconium alloying agent to each melt in order to maintain a full zirconium content. Transfer of such a melt to a separate crucible is followed by a rapid reduction in the soluble zirconium content, and in consequence it is essential, if a full zirconium content is to be obtained, for castings to be poured from the crucible in which the final zirconium alloying is performed. A full zirconium content improves tensile properties and castability, and reduces microporosity; and for these reasons the zirconium casting alloys\*\* developed in this country have always contained the full zirconium content. Some loss of soluble zirconium content occurs on melting, so that the remelted alloys require revivification with additional zirconium alloying agent before pouring.

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§ Pressure die-castings are dealt with elsewhere (H. J. Sharp, *J. Inst. Metals*, 1956–57, 85, to be published).

|| Discovered by F. Sauerwald, who has recently published a comprehensive bibliography on magnesium–zirconium alloys.<sup>4</sup>

¶ See British Patent No. 511,137. Elements which precipitate zirconium in this way are termed "alloying inhibitor elements", those which do not do so being termed "permissible elements".

\*\* For convenience, magnesium alloys containing zirconium may be referred to simply as "zirconium alloys".



Alloying directly with zirconium metal is inconvenient and expensive, and the element is normally introduced via proprietary salt mixtures containing  $ZrF_4$  or  $ZrCl_4$ , or by "master alloys" prepared by a preliminary reaction between salt mixtures and magnesium, with elimination of the bulk of the halide reaction product.

The alloys containing zirconium fall into two groups, the high-strength alloys Meltron\* Z5Z, RZ5, and TZ6, and the high-temperature alloys Meltron ZRE1, MCZ, and ZT1 (Table I).

In the high-strength alloys, the tensile properties are due to zinc, and are realizable because of the grain-refining action of the zirconium and its marked effect in increasing the solid solubility of zinc in magnesium.† Alloy RZ5 contains an addition of rare-earth metals (Mischmetall‡) which largely suppresses the slight tendency of Z5Z to exhibit microporosity, particularly in complex castings, and confers weldability on the alloy. The thorium in TZ6 alloy exercises similar effects and enables a higher zinc percentage to be utilized without appreciable microporosity or reduced ductility, thus permitting development of enhanced tensile properties. The high-temperature group of alloys contain relatively high contents of rare-earth metals or thorium, and it is on these additions that creep-resistance at elevated temperature depends. These alloys are also characterized by absence of microporosity, always provided that a full zirconium content is present; and for this reason the alloy ZRE1 has been extensively used for normal-temperature applications where pressure-tightness is essential.

All the zirconium alloys used in this country develop their full mechanical properties with a precipitation heat-treatment at relatively low temperatures. Elsewhere, alloys with low zirconium or high zinc content have been developed which require high-temperature solution-treatments,<sup>5, 6</sup> but these do not appear to be sufficiently widely used to justify separate consideration.

## 2. ALLOYS CONTAINING ALUMINIUM

These alloys contain aluminium, zinc, and small amounts of manganese (see Table I), the function of the last being to increase the corrosion-resistance by largely suppressing the adverse effect which the iron present would otherwise exert. Tensile properties are improved by solution-treatment or by full heat-treatment, and are very dependent on grain-size. This is generally controlled by some form of carbon-inoculation treatment or by the well-known procedure of superheating the melt for a period to temperatures above about 850° C.

Although gas is not normally a serious problem in these alloys, departure from good melting practice can lead to gas pick-up, with consequent porosity in castings.§ Degassing of magnesium melts is therefore frequently practised.

\* Meltron and Elektron are registered trade marks of Magnesium Elektron, Ltd.

† The freezing range of the magnesium-4½% zinc alloy is reduced from approximately 300° to 90° C. on adding zirconium to make the alloy Z5Z.

‡ "Mischmetall" is the commercial mixture of the cerium group of rare-earth metals and contains approximately Ce 50, La 25, Nd 18, Pr 7%.

§ This is very different from gas porosity in aluminium-base alloys and takes the form of intergranular cavities hardly distin-

High-purity versions are available of some of the aluminium-containing alloys || which, by limitation mainly of the iron and nickel contents, show increased resistance to corrosion. The main practical problem here is to avoid pick-up of impurities during processing.

In Great Britain, it is usual for magnesium alloy castings to be made by remelting ingot of the desired composition together with normal process scrap. Thus, castings to be released to B.S. (Aircraft) and D.T.D. specifications are made from approved ingot and the founder's own scrap, and the founder is required to check the composition of only a proportion of the melts. In other countries, different practices and inspection procedures sometimes apply.

It is general practice to melt in steel crucibles of 50–600 lb. capacity, and the metal is poured direct from the crucible into the mould in the case of sand castings. For gravity die-castings, lip-axis tilting crucible furnaces are commonly used, although bale-out furnaces are also employed.¶

Sand castings at present in production vary in fettled weight from a fraction of an ounce to about 15 cwt. and include some of the most complex shapes ever attempted. An example is the aircraft supercharger casing shown in Fig. 1 (Plate XLIII) weighing about 360 lb. and incorporating over 50 cores. Gravity die-castings are normally of much lower maximum weight, although a few very massive castings of simple shape have been made in metal dies where this has proved more convenient than the use of sand moulds.

In what follows, attention is directed primarily to sand castings, points of special relevance to die-casting being given in Section VII.

## III.—CONTROL OF MELT QUALITY

In this section, important practical points relating to the quality of melts of alloys containing zirconium and aluminium are first dealt with separately, followed by points on fluxing procedure applicable to all magnesium alloys. Check tests for metal quality are then considered.

### 1. ALLOYS CONTAINING ZIRCONIUM

In the early days of magnesium-zirconium alloys difficulties with new types of persistent flux inclusion were encountered, which were solved by the development of special alloying salt mixtures<sup>7, 8</sup> and "heavy" fluxes.<sup>9</sup> It will be assumed in what follows that appropriate alloying materials and fluxes are being employed.

#### (a) Attainment of Desired Composition

Special points arise in connection with zirconium, rare earth metals, and thorium.

guishable microscopically from microshrinkage due to imperfect feeding. The latter results partly from the wide freezing range of 180° C. under foundry (non-equilibrium) conditions, which may be compared with freezing ranges of 90°–95° C. for the zirconium-containing alloys Z5Z, ZRE1, ZT1.

|| So far specifications have been issued for A8 only (D.T.D. 684/690).

¶ Techniques whereby the metal is pumped through steel pipes to metal moulds have also been developed, notably in the U.S.A., but few structural castings are yet produced in this way.

TABLE I.—Designations, Compositions, and Tensile

Alloy Type	Designation (U.S. equivalents in parentheses)*	Specification	Chemical Composition, %					
			Al	Zn	Mn	Zr	Rare-Earth Metals	Th
High-strength Zirconium	Z5Z (ZK51) { As cast Heat-treated	D.T.D. 711A D.T.D. 721A	} ...	3.5-5.5 4.5	0.15 (max.)	0.4-1.0 0.7	...	...
	RZ5 (ZE41) { As cast Heat-treated	D.T.D. 738 D.T.D. 748		3.5-5.0 4.0	0.15 (max.)	0.4-1.0 0.7	0.75-1.75 1.2	...
	TZ6 (ZH62) Heat-treated	D.T.D. 000 (Draft M40)		5.2-5.8 5.5	0.15 (max.)	0.4-1.0 0.7	0.1 (max.)	1.5-2.0 1.8
High-Temperature Zirconium	ZRE1 (EZ33) As cast and annealed	D.T.D. 708	...	0.8-3.0 2.2	0.15 (max.)	0.4-1.0 0.6	2.5-4.0 2.7	...
	MCZ (EK31) As cast and annealed	D.T.D. 728	...	0.2 (max.)	0.15 (max.)	0.4-1.0 0.6	2.5-4.0 3.0	...
	ZT1 (HZ32) Heat-treated	D.T.D. 5005	...	1.7-2.5 2.2	0.15 (max.)	0.4-1.0 0.7	0.1 (max.)	2.5-3.5 3.0
Standard Aluminium-Containing	A8 { As cast Solution-treated	{ B.S. L121 (Aircraft) B.S. 1277 (Gen. Eng.)	{ 7.5-9.0 8.0	0.3-1.0 † 0.5	0.15-0.4 † 0.3	...	...	...
		{ B.S. L122 (Aircraft) B.S. 1278 (Gen. Eng.)						
	A8 (high-purity) { As cast Solution-treated	{ B.S. 1278 (Gen. Eng.) D.T.D. 684	{ 7.5-9.0 8.0	0.3-1.0 0.5	0.15-0.4 0.3	...	...	...
		{ D.T.D. 690						
	AZ91 ** { As cast Solution-treated Fully heat-treated	{ B.S. L123 (Aircraft) B.S. 1273 (Gen. Eng.)	{ 9.0-10.5 9.5	0.3-1.0 † 0.5	0.15-0.4 † 0.3	...	...	...
		{ B.S. L124 (Aircraft) B.S. 1274 (Gen. Eng.)						
		{ B.S. L125 (Aircraft) B.S. 1275 (Gen. Eng.)						
		{ ...						
	C †† { As cast Solution-treated Fully heat-treated	{ ...	{ 7.5-9.5	0.3-1.5	0.15 (min.)	...	...	...
		{ ...						

Single figures indicate nominal composition within the specified ranges.

\* Suffixes denoting state, &amp;c. are omitted.

† According to B.S. 1273, 1274, 1275, 1277, and 1278, the zinc content is 1.0% max., the manganese content 0.2-0.4%, and the maximum copper and silicon impurities are 0.2% and 0.4%, respectively. Nickel is not specified. In addition, if the zinc content is less than 0.3%, it is advisable that the copper content should be less than 0.1%.

‡ Specified in B.S. 1273, 1274, 1275, 1277, and 1278.

*(i) Zirconium*

To achieve a full zirconium content, the following points are important:

(a) Avoidance of contamination with alloying inhibitor elements and in particular with aluminium-containing alloy scrap.\* Adhering moulding sand, corrosion product, &c., should be removed from scrap, preferably by shot-blasting, before charging to the melt.

(b) Proper performance of the zirconium alloying process and assessment of the effective soluble zirconium content of the melt before casting. The latter is best checked by the appearance of the fracture of a 1-in.-dia. chill bar † cast from the metal.<sup>3, 10</sup>

(c) Close temperature control between the completion of zirconium introduction and pouring. (Below about 750° C., zirconium is lost relatively rapidly from melts alloyed at about 800° C. in the normal manner. On the other hand, if the melt temperature rises much above

about 830° C., there is a risk of zirconium loss owing to iron pick-up from the steel crucibles normally employed. In particular, alloying should not be carried out above 830° C.)

With the proprietary "master-salt" process for introducing zirconium,‡ the salt, which is charged to the crucible in lumps, reacts with the metal to form a stiff, pasty mass from which the zirconium is liberated by a few minutes' puddling of the melt. During this procedure, flux is applied to the metal surface as required to prevent oxidation of the metal, and the puddling achieves the same objects as the rotary flux-refining step applied to the alloys which do not contain zirconium (Section III. 3).

Apart from the refining stage, the inspissated all-purpose flux, HE,§ used by Magnesium Elektron, Ltd., and its associates for zirconium alloys, is employed in exactly the same manner as are the fluxes for non-

\* Steps should be taken to make contamination with alloys containing aluminium as nearly physically impossible as is practicable.

† Periodic shot-blasting of the chill mould is desirable to

maintain the full chilling effects.

‡ Zirmel master-salt is based on ZrF<sub>4</sub>.

§ This flux corresponds in general composition to flux (f) of British Patent No. 652,234.



## Properties of Magnesium-Base Casting Alloys.

Chemical Composition, %						Tensile Properties			Descriptive Remarks
Pb (max.)	Sn (max.)	Fe (max.)	Cu (max.)	Si (max.)	Ni (max.)	0.1% $\frac{1}{2}$ Proof Stress, tons/in. <sup>2</sup>	Ultimate Stress, tons/in. <sup>2</sup>	Elongation on 2 in., %	
...	...	0.01	0.03	0.01	0.005	7.0-8.5 8.5-10.5	13.0-17.0 15.0-18.0	7-15 5-12	Normal high-strength Zr alloy. Non-weldable. May crack under high re- straint.
...	...	0.01	0.03	0.01	0.005	5.5-6.5 8.0-9.0	11.0-12.0 13.0-14.5	3-6 3-5	Weldable. Almost porosity-free. Resistant to cracking.
...	...	0.01	0.03	0.01	0.005	9.5-11.0	17.0-19.5	5-15	Highest-strength alloy. Weldable. Almost porosity-free. Crack-resistant.
...	...	0.01	0.03	0.01	0.005	5.0-6.0	9.0-11.0	3-6	For use up to 250°C. Excellent castability. Weldable. Completely pressure-tight.
...	...	0.01	0.03	0.01	0.005	5.0-6.0	9.0-10.5	3-6	Crack-resistant.
...	...	0.01	0.03	0.01	0.005	5.0-6.0	12.0-14.0	5-10	For use up to nearly 350°C. Weldable. Completely pressure-tight. Crack-re- sistant.
0.1 ‡	0.1 §	0.05	0.15 †	0.30 †	0.01 †	4.5-5.5 4.5-5.5	9.0-11.0 13.0-17.0	2-5 6-15	General-purpose alloy. Good shock-resistance as solution-treated.
0.005	0.005	0.003	0.005	0.01	0.001	As for A8			Enhanced corrosion-resistance.
0.1 ‡	0.1 §	0.05	0.15 †	0.30 †	0.01 †	4.5-6.0 5.0-6.0	8.0-10.5 13.0-16.0	1-3 4-8	General-purpose alloy for intricate cast- ings.
...	...	0.05	0.35	0.4	0.02	6.5-8.5 4.0-5.5 4.0-5.5 5.0-7.5	13.0-16.5 8.0-11.0 12.0-16.0 13.0-16.0	1-4 2-5 4-10 1-3	Low ductility when fully heat-treated. General-purpose alloy for commercial applications.

In the ranges for tensile properties, the lower figure is usually the specification minimum.

§ According to B.S. 1273, 1274, 1275, 1277, and 1278, the tin content is 0.3% max.

|| According to B.S. L121, L122, L123, L124, and L125, the total impurities of iron, copper, silicon, and nickel are limited to 0.4% max.

¶ Proof stress by "offset" method.

\*\* AZ91 is also available in the high-purity grade.

†† Proposed for B.S.I. General Engineering Specification. Total iron, copper, silicon, nickel = 0.75% max.

zirconium alloys. It is chemically balanced in such a way as to exhibit the beneficial properties of  $MgCl_2$  in preventing and extinguishing burning, but can yet be used on alloys containing rare-earth metals without undue loss of the rare-earth-metal content. Fluxes free from  $MgCl_2$  are available, but although these prevent burning from starting if properly applied, they are noticeably less effective in extinguishing oxidation once it has been allowed to begin.

## (ii) Rare-Earth Metals

Losses of rare-earth metals from molten alloys through oxidation are inappreciable even if much burning is allowed to occur, but oxidation of incompletely melted metal can lead to loss of rare earth metals owing to preferential oxidation of the low-melting  $\beta$  phase. To maintain the rare-earth metal content of alloys such as ZRE1 on remelting and processing, it is convenient to replace some of the normal master-salt addition with a proprietary salt, "Zirmel 2",\* which in addition to

liberating zirconium also counteracts the loss of rare-earth metals which would otherwise occur.

## (iii) Thorium

Thorium is readily lost from molten alloys if oxidation is allowed to occur, and vigilance is required to prevent oxidation at all stages of melting and puddling by timely application of flux. A special flux, TE,† is available which is more effective than HE in minimizing processing losses. Even so, the thorium content of ZT1 alloy is likely to be lowered about 0.2% on remelting and puddling, and an appropriate addition of thorium should be made to the melt. Thorium is normally added as a hardener alloy with magnesium, containing about 20% thorium and 2¼% zinc.

## (iv) Impurities

In alloys containing zirconium, the contents of alloying inhibitor elements will of necessity be very low, except

\* This material contains reducible zirconium and rare-earth halides.

† Corresponding in general composition to flux (a) of British Patent No. 652,234.

close to the bottom of the melt; \* the question of their control does not arise, therefore, so long as difficulties are not encountered in alloying the zirconium.

Nickel exerts relatively little influence on the corrosion-resistance of the zirconium alloys, and as this element is a partial alloying inhibitor for zirconium, it is unlikely to reach objectionable concentrations in practice.

In the thorium alloy, ZT1, the rare-earth-metal content must not exceed about 0.1% if the maximum resistance to creep and corrosion is to be achieved. Avoidance of contamination with ZRE1 is therefore important, though the flux recommended for ZT1 alloy, namely TE, is able to remove rare-earth-metal impurities to a useful extent.

#### (b) Other Considerations

The question of gas content hardly arises with zirconium alloys, since, even if corroded ingot is melted, test castings show little if any increase in porosity, provided that a full zirconium content is attained in the melt. The excess hydrogen is presumably precipitated as an insoluble zirconium hydride.† However, it is advisable to minimize hydrogen introduction into the melt, since this leads to unnecessary consumption of zirconium. Thus corroded scrap should be cleaned (e.g. by shot-blasting) before melting, and reasonable precautions taken to avoid moisture pick-up in the various salts and fluxes, all of which are hygroscopic.

## 2. ALLOYS CONTAINING ALUMINIUM

### (a) Attainment of Desired Composition

Special points arise in connection with manganese content and with the control of impurities in the high-purity version (D.T.D. 684/690) of A8 alloy.

#### (i) Manganese

Little change in manganese content occurs on remelting unless the initial content is well above the solubility limit for manganese in the liquid alloy (about 0.25% for A8 at 650° C.), in which case some reduction of the manganese content may occur through settlement of insoluble Mn-Al particles. This is of little practical consequence, however, since it is the dissolved manganese which is beneficial to the corrosion-resistance, and the total manganese will remain above the specification minimum of 0.15%.

Manganese is readily added to magnesium either by means of  $MnCl_2$  or as a hardener alloy with aluminium, so that if for any reason a deficiency is present in a melt, e.g. if some metal with high aluminium or zinc content

has been diluted with pure magnesium, the manganese content can be easily adjusted. A manganese efficiency of about 75% may be expected when alloying with  $MnCl_2$ , the balance of the manganese entering the flux phase as fine particles of the pure metal.

#### (ii) Impurities

Impurities which may require attention when scrap or secondary metal are being incorporated in melts are copper, nickel, silicon, and tin. None of these is very easily removed from magnesium-aluminium alloys, so care should be taken to ensure that the scrap added will not introduce objectionable amounts.

The same position applies even more strongly with high-purity alloys, in which the iron content has also to be kept to a low limit (0.003% in castings or 0.002% in ingot).‡ It is necessary here to avoid making the melt hotter or heating it longer than is strictly necessary, and "seasoned" crucibles<sup>11</sup> should be used. Grain refinement should be by carbon inoculation. Fluxes of low iron content are unnecessary.<sup>11</sup>

#### (b) Grain-Size

The alloys are normally supplied in the form of reasonably fine-grained ingot, and the scrap added to melts is likely to be fine grained, but it is a desirable precaution to apply a grain-refining step to each melt from which castings are to be poured. Originally melts were "superheated" by holding at temperatures in excess of 850° C. for a period,§ but the carbon-inoculation processes enable fine grain to be achieved without raising the melt above normal casting temperatures.|| Hexachlorethane and hexachlorbenzene<sup>16</sup> are useful inoculants and exert a slight degassing action where the gas content of the melt is initially excessive. About 0.025–0.1% of the grain-refining agent is placed in a suitable perforated diving bell and plunged into the metal at about 750° C. A projection below the bell is useful to prevent contamination of the degassing agent with flux at the bottom of the crucible. These chlorinated hydrocarbons have no refining action on the melt<sup>17</sup> other than that of carbon inoculation, and in fact may give rise to a certain amount of drossy scum on the metal surface which requires removal or absorption with flux. Other methods of carbon inoculation involve the use of mixtures of paraffin wax with  $CaF_2$ <sup>18</sup> and flux with lamp black.

If desired, a check on grain-size can be made by sand casting a D.T.D. (B.S. L101, Fig. 1) or similar test-bar and examining the appearance of the fracture in comparison with those from bars of known grain-size. The grain-size in a D.T.D. bar should not be coarser than about 0.15 mm.¶ Should a coarse fracture be obtained,

\* For example, the solubilities of iron and aluminium in magnesium saturated with zirconium do not exceed 0.002%, so that until the contents of these impurities have been reduced by precipitation with zirconium down to this level, full grain refinement of a melt cannot be achieved. The precipitated impurities rapidly settle to the bottom of the melt.

† Complete removal of dissolved zirconium is possible by passing hydrogen through the melt.

‡ D.T.D. Specification Nos. 684/690. The iron tolerance limit for good corrosion-resistance in A8 alloy appears, however, to be 0.005%.<sup>15</sup>

§ The mechanism of grain refinement by superheating is not yet wholly clear,<sup>12, 13</sup> but there is some evidence that it may be

due to nucleation by  $Al_4C_3$ .<sup>14</sup> Thus, the effect is observed only with alloys containing aluminium; superheating is accompanied by surface decarbonization of the steel crucibles used; metals which form stable carbides, such as beryllium, zirconium, and thorium, suppress grain refinement on superheating; and these metals also interfere with grain refinement by the carbon-inoculation processes which, in this country, have largely superseded superheating.

|| Superheating is, however, still practised quite widely in the U.S.A.

¶ A short solution-treatment greatly facilitates grain-size determinations on these alloys without inducing appreciable grain growth.



further addition of grain-refining agent is indicated, but it is possible that contamination of the melt with zirconium alloy has occurred, in which case further additions may be unsuccessful in giving a fine grain. If this happens, the melt can either be cast off into ingot for adding in small amounts to other melts, or it may be transferred into a clean hot crucible, where it should be possible to grain refine it satisfactorily with further carbon additions.\*

### (c) Gas Content

The amounts of gas arising in magnesium alloy melts during normal processing of clean ingot and scrap are not of great practical consequence, but the melting of corroded ingot or scrap, use of wet flux, &c., may lead to microporosity directly attributable to gas. By giving rise to outcropping microporosity, one of the conditions is provided for a certain type of flux inclusion to arise (Section VI. 3). In the most severe cases, "worm-hole" castings, with the metal rising in the feeder heads as solidification proceeds, provide clear evidence of gas. In less severe cases, however, microporosity is encountered, particularly in thick sections, which is hardly distinguishable<sup>19</sup> from that due to imperfect feeding, so that the cause may not be readily apparent.† Degassing of magnesium melts is therefore wise, and, although in many melts it probably has little beneficial effect, it does at least tend to correct errors in melting and thus provide a more uniform quality of metal.

The most effective degassing is provided by bubbling chlorine through the melt at 720°–780° C.,<sup>21, 22</sup> and this has been combined with carbon grain refinement by prior passage of the gas through CCl<sub>4</sub>.<sup>23</sup> The chlorine is in any case usually led into the melt through a carbon tube, and even in the absence of CCl<sub>4</sub> is found to induce some grain refinement. In practice, the use of hexachloroethane for grain refinement will effect sufficient degassing, in conjunction with good fluxing techniques,‡ to avoid gas troubles.

## 3. FLUXING PROCEDURE

The whole process of melting and fluxing of magnesium alloys has been discussed in considerable detail elsewhere,<sup>17</sup> and an account has been given of the Elektron technique.<sup>2</sup> Modern fluxes permit wide latitude in actual procedure and very little care is required to ensure freedom from flux contamination in the final castings. In the non-zirconium alloys, any flux (or oxide) inclusions found in castings will have arisen at the pouring stage and will not have been present as such in the melt before pouring.§ Nevertheless, certain precautions can be taken

at the melting and fluxing stages which minimize the risk of flux inclusions arising during subsequent casting, however little care is taken in cleaning the pot and the metal surface before pouring. Of the following points, (1), (2), (6), and (7) apply equally to the zirconium alloys. (As already indicated, a rotary "refining" process is not applied to zirconium alloys, since the same objects are achieved in the puddling process used to introduce the zirconium.)

(1) The flux should be used to prevent burning rather than to extinguish it once it has been allowed to begin.

(2) Crucibles should not be too full, otherwise it will be difficult to carry out the rotary refining step satisfactorily. The metal level should be at least 3–6 in. below the lip, according to the size of crucible; it should also be well below the beginning of the recess of the pouring lip to permit adequate cleaning.

(3) If a two-flux process including a fluid Z-type (protective) flux for melting is employed, care should be taken to see that unabsorbed fluid flux does not remain on the metal surface in contact with the pot wall. (This can arise if excessive Z flux is used in melting or if the Z flux is stirred into the melt, and insufficient inspissated E flux subsequently applied.)

(4) The step of "refining" the melt by rotary stirring for a minute or so with an inspissated E-type flux is valuable and performs the following functions:

(i) The rotation of the metal brings to the surface any excess fluid flux coating the sides of the crucible slightly below the metal level, so that such flux is rendered harmless, either by absorption into the inspissated flux cover during stirring, or by subsequent application of flux when stirring has ceased.

(ii) In stirring, some of the inspissated flux becomes distributed over the bottom and sides of the crucible, where it is able to absorb and to some extent immobilize excessive protective flux already there.

(iii) If oxidation has been allowed to occur during melting, the stirring will bring to the metal surface, in the form of glowing embers, oxide loosely adhering to the crucible walls, whilst oxide at the bottom of the melt is absorbed and immobilized by the flux stirred through the melt.

(5) During the refining process, a gentle sprinkling of flux should be applied as required to avoid oxidation. It is quite unnecessary to stir most or all of the flux applied down through the metal.¶ If, through burning during melting, a thick layer of oxide or dross has accumulated on the metal surface by the time refining is to be carried out, this should preferably be covered with flux

\* Unless the metal is transferred into a separate crucible, the presence of the insoluble Zr–Al particles at the bottom of the melt will prevent grain refinement, probably owing to co-precipitation of carbon (a zirconium alloying inhibitor element) on to the zirconium-rich particles. Similarly, zirconium–aluminium alloy, although itself incapable of introducing a measurable soluble zirconium content into magnesium–aluminium alloy, will remove the alloying inhibitor elements phosphorus and iron from magnesium–aluminium alloy melts down to a very low level.

† It has been claimed that completely degassed magnesium–aluminium alloy melts do not exhibit visible microporosity,<sup>20</sup> but sand castings from melts given a prolonged chlorine treatment can nevertheless show microporosity in underfed sections.

‡ Where dirty or fine scrap is present in the charge, it is particularly necessary to add sufficient flux to absorb the

hydroxide or hydrated oxide corrosion product and to render the flux residue as a whole sufficiently fluid to enable the metal to come in contact with and so dehydrate the whole of the residue. If lumps of unwetted oxide are present in the residue, they will act as a reservoir of hydrogen, and gas will re-enter the melt from the residue after the degassing step has been applied.

§ Flux inclusions can arise in zirconium alloy castings from the use of unsuitable alloying salts and fluxes, or if insufficient metal is left in the crucible after casting.

¶ The fluxes used for magnesium are heavier than the metal when freshly melted and so will sink in the melt on penetration of the meniscus. Exposure to the air causes drying of the flux cover through hydrolysis, with some reduction in apparent density.

and removed (especially with zirconium alloys) or else sufficient flux should be added during refining to absorb the oxide. A small quantity of flux remaining on the metal surface after refining need not be removed, but a large quantity is preferably removed before the final *E*-flux cover is applied.

(6) Before applying the final *E*-flux cover, it is desirable to scrape the inside of the crucible on the pouring side and the lip down to the level of the metal and then to cut away any flux adhering to the crucible wall under the pouring lip at and immediately below the metal level. "Sludging the pot",\* although sometimes practised, is neither necessary nor desirable.

(7) If the melt has had to stand after refining for an abnormally long time and the flux cover has thereby become brittle and powdery, it is best removed with a ladle and a fresh cover applied.

A very good indication of how well melting and fluxing have been carried out is provided in the case of non-zirconium alloys by the state of the crucible residue after casting. This should be about 4-7% of the weight of metal melted and should not itself contain more than 15% metal. It should be pasty in consistency and fairly stiff, and should show little tendency to flow when the crucible is tipped up. No unwetted oxide should be visible, and burning should not occur when the crucible residue is scraped out. Similarly, burning of residual metal adhering to the crucible walls should not begin as the walls become exposed during casting, since with proper fluxing the walls will be wetted with flux.

#### 4. CHECK TESTS FOR MELT QUALITY

##### (a) Chemical Composition

Sampling of melts for chemical or spectrographic analysis may be carried out using the copper-chilled carbon mould described by Wilkinson and Hirst,† in which case a section about  $\frac{1}{8}$  in. from the chilled end probably represents the best surface for spectrographic analysis so far as possible segregation of aluminium is concerned. For spectrographic analysis alone, a heavily chilled splash sample appears generally preferable, and this applies in particular to ZRE1 alloy which can develop appreciable segregation in the chilled carbon mould.

Suitable methods for the determination of all alloying elements and likely impurities have been published.‡

In zirconium alloys, the appropriate D.T.D. specifications call for a minimum "available zirconium" content of 0.4% and give a method for its determination which involves dissolving the sample in dilute HCl. Such chemical methods provide only an approximate separation of metallographically soluble and insoluble zirconium present in the sample, and therefore do not give a satisfactory measure of the effective soluble zirconium content of the original melt, which corresponds to the

zirconium dissolved in the molten alloy and is reflected in the grain-size and tensile properties of metal cast from it. An "available zirconium" content in accordance with specification requirements is therefore no guarantee of an adequate zirconium content. The latter is indicated in the first instance by a satisfactory fracture test, backed up if desired by a grain-size determination, and by satisfactory tensile properties on sand-cast test bars.

##### (b) Mechanical Tests

Tensile tests made on separately cast bars in accordance with B.S. L101 provide, of course, a valuable *post hoc* check on melt quality. The D.T.D. bar does not, however, appear wholly suited to magnesium, since the results obtained depend to an undesirable extent on the skill of the operator, and a horizontally cast bar partially shaped appears preferable, particularly for the zirconium alloys.

No instances appear to have arisen with magnesium alloys where routine mechanical tests other than tensile tests have proved desirable. Thus, although the alloy ZRE1 is frequently employed at elevated temperatures on account of its excellent creep-resistance, experience has shown that if the analysis of a ZRE1 melt is correct and the room-temperature tensile properties on separately cast test-bars are satisfactory, castings made from the melt will show good creep-resistance.‡ Stress-rupture tests on bars taken from the melt are both unnecessary and potentially misleading.

##### (c) Use of Special Test Castings

Not infrequently the foundryman blames the quality of the metal for casting defects, and it is often difficult to provide contrary evidence to his satisfaction. To this end, a test pattern, designed to be susceptible to changes in metal quality and on which sensitive radiography can readily be carried out, can prove a more valuable guide than the standard tensile bar.

## IV.—CONTROL OF CASTING

### 1. POURING

This is normally the only stage of the whole process at which there is any risk of flux inclusions arising, and it is also one at which oxide inclusions can be produced. As a consequence, pouring is worthy of craftsmanship; yet it is not uncommon to see foundries where real care is taken in melting and moulding, but where the flux cover is roughly pushed back before casting, the melt allowed to oxidize before application of sulphur is begun, and the metal then "slopped" into the mould. For better control of quality, attention should be paid to the following points during pouring and preliminary cleaning.§ (It is assumed that the pouring temperature is controlled either by lifting the crucible from the furnace with the

\* Removal of the flux residue from the bottom of the crucible with a perforated ladle. The low density of magnesium causes impurities to collect at the bottom rather than at the top of a melt.

† Appendix to ref. (3). British Acheson petroleum cake carbon, with thermal conductivity 8 B.Th.U./hr./ft.<sup>2</sup>/°F./ft., is suitable. Graphite should not be used. The chill plate should be at least

1 in. thick.

‡ The level of properties obtainable in actual castings is briefly indicated in Section IX.

§ The conditions under which normal care in cleaning may not suffice to prevent inclusions, and the special precautions which may be required under exceptional conditions, have been discussed elsewhere (see ref. (17), pp. 446-7 and Appendix III).



metal at a predetermined temperature above the desired temperature (e.g. 20°),\* or else at an appreciably higher temperature, so that a pyrometer can be inserted and the melt allowed to cool near the mould until the right temperature is reached.)

(i) Handle the crucible carefully so as not to break up the flux cover unnecessarily. (If burning of the metal surface is in progress by the time the crucible has reached the mould, this can be suppressed with a *very* light sprinkling of *E*-type flux, or application of sulphur/5% boric acid † mixture, dusted from a muslin bag.)

(ii) Before pouring, scrape the inside of the lip and pot walls on the pouring side and preferably brush the outside with a wire brush. Also remove loose scale and flux from the crucible lugs and lifting hooks.

(iii) In cleaning the metal surface, begin dusting sulphur before the flux cover is touched.

(iv) The flux cover must be gently pushed back along the metal surface for some distance from the pouring lip whilst dusting of sulphur is continued; any flux adhering to the crucible walls near the lip at the metal level should be drawn back in the process. This cleaning of the metal surface is conveniently done when the crucible has been tilted so that metal is about to enter the lip recess. If a high pouring temperature is being employed, cleaning should be done under a sulphur/boric acid dusting, although plain sulphur is preferable for application to the falling metal stream itself.

(v) The crucible lip should be brought as close as possible to the pouring box of the mould, the mould being raised if necessary to a suitable level above the floor. Lip-axis tilting would seem desirable, but does not appear to be used in practice.

(vi) Pouring should be as slow and smooth as possible consistent with rapidly covering the top of the down-gates and gradually raising the metal in the pouring box to the desired level. To minimize turbulence, a rectangular rather than a round or oval box is desirable, and the size should be adjusted to the size of the down-gates; smooth, steady pouring is unlikely to be achieved in practice if large boxes are fitted to small castings, or vice versa.

(vii) Avoid allowing the metal to fall vertically to the bottom of the pouring box. If rectangular pouring boxes are used, this can conveniently be achieved by banking up the back of the box with moulding sand to provide a shallow channel for the metal.‡ (This precaution can greatly reduce the chance of oxide skin inclusions in alloys containing rare-earth metals, such as ZRE1.)

(viii) In pouring a number of castings from the same crucible, avoid tilting the crucible back to the vertical between each pour. The crucible should be maintained as far as possible at the appropriate angle, and if necessary the metal should be lightly skimmed before pouring each casting.

(ix) Leave some metal unpoured in the bottom of the crucible. For zirconium alloy melts, this should be from one-fifth to one-tenth of the charge, depending on the

crucible size and the rate of pouring. These alloys exhibit a settled layer of loosely packed clusters of zirconium-rich particles which render the metal at the bottom of the crucible viscous and liable to entrap globules of flux of various sizes which may become separated from the main body of the salt phase during the alloying process.§ The metal remaining in the crucible can be cast off into ingot and added to subsequent melts. Where large castings are being poured "two up" (i.e. from two crucibles simultaneously), it is obviously necessary to check that sufficient metal is left in *each* crucible after pouring.

## 2. MOULDING SAND

### (a) General Considerations

The properties of magnesium which are most important in determining the characteristics required of the moulding sand are chemical reactivity and low density.

Since normal foundry sands contain clay and water to make them mouldable, inhibitors must be added to prevent reaction between magnesium and the moisture present. The inhibitors employed are volatile at the casting temperature and must therefore not be used excessively, or difficulties will arise with "blows" or misruns accentuated by the low density of magnesium. For the same reason, the sand must have a high permeability. The amount of inhibitor required will depend on the water content of the sand, which in turn is largely dependent on its clay content.

The majority of magnesium sand castings are made in washed silica sand bonded with bentonite and with a moisture content of 2-3%. Typical inhibitors for this type of sand are sulphur (about 4%) and boric acid (about ½%). Some foundries prefer to use natural sand, since this is more readily mouldable than "synthetic" sands and the initial cost is lower. Natural sands may, however, have widely varying clay contents (e.g. 8-12%), and so require higher water contents (e.g. 6%) to render them workable, and consequently higher sulphur contents (e.g. 6%) to eliminate mould reaction. Care is required to avoid under-inhibition of natural sands, since it is possible for an excess of moisture to be present without this being evident from the moulding behaviour. Other inhibitors, such as ammonium bifluoride, ammonium borofluoride, and urea, are also used, and it is common practice to add small amounts of diethylene glycol to reduce "drying out", a failing to which synthetic sands are prone. Data on some typical moulding sands for magnesium are given by Partridge,<sup>27</sup> and American practice has been recently reviewed.<sup>22</sup>

### (b) Control of Moulding Sand

The above brief description of magnesium moulding sand indicates the basic requirements for control of quality. The tests applied in different foundries vary considerably in accordance not only with the type of work, equipment, and labour available, but also with the attitude shown to scientific methods of testing as opposed

\* It must be remembered that the rates of cooling may be very different if the crucible is lifted with a rising or falling temperature.

† Unlike plain sulphur, this puts a protective film on a clean metal surface.

‡ See ref. (17), Fig. 2 (p. 447).

§ If alloying is carried out with  $ZrCl_4$ , or chloride salt mixtures containing this salt, but in the absence of about 20% of  $BaCl_2$ , the salt reaction product of the alloying reaction becomes associated with the zirconium-rich particles themselves and the castings produced show persistent chloride contamination.<sup>7</sup>

to the "feel" of the sand. Some aspects of mould preparation must perhaps be left to the control of the individual moulder, but certain positive steps such as the following can be taken with a view to achieving high-quality castings and minimizing scrap:

- (1) Ensure that control of raw materials is adequate.

Sand: The following tests can usefully be carried out on new deliveries:

Grain-size (which should be sufficiently coarse to give the desired permeability without poor surface finish).

Clay content (if a natural sand).

Moisture content.

Clay: Occasional analysis and physical tests.

Inhibitors: Occasional analysis.

- (2) Ensure that milling and mixing are thorough, both by provision of suitable equipment and application of appropriate routine tests.

- (3) Avoid accidental contamination with foreign materials, e.g. coal dust,\* flux,† &c.

- (4) Ensure correctness of composition and properties of batches of moulding sand. The following tests are appropriate and, where possible, are best done on the spot:

Moisture content: On each batch. Several rapid methods are available. A good indication of moisture content can be obtained by "feel", provided other factors are reasonably constant. In practice, adequate control of each milled batch may be achieved by "feel", if periodic checks are made by more precise methods.

Inhibitor content: Periodic checking by chemical analysis.

Permeability: Periodic checking.‡

Green strength: Periodic checking.‡

Dry strength: Determinations may be required for core sand, the importance depending on the type of core binder employed.

Water-soluble salts (other than inhibitors such as boric acid): An occasional chemical check is desirable, since their presence can lead to mould reaction even when normal moisture and inhibitor contents are present. In normal practice, however, the amount of new sand added to the system is adequate to avoid build-up of these salts from the inhibitors.

#### (c) *Some Moulding Considerations*

Other aspects of mould preparation which require brief consideration, but are not readily amenable to numerical assessment and control, are mentioned below.

##### (i) *Hardness of Ramming*

Mould "hardness" is obviously important in affecting permeability, and hard ramming can give rise to various

defects. Although moulding practice must to a large extent be left to the individual moulder, some degree of control is possible by the use of hardness-measuring devices. In machine moulding, rather closer control is possible by ensuring correct operation of the equipment, although the majority of work still requires considerable moulding skill. Box bars are useful in reinforcing lightly rammed sand moulds against collapse, but instances have occurred where contraction has been restrained by the bars, leading to cracked castings.

##### (ii) *Venting*

Proper venting of moulds is most important, particularly for avoiding misruns in thin sections.

##### (iii) *Skin Drying of Moulds*

It is common practice to "skin dry" moulds before they are closed, this normally being carried out manually with a gas torch. If excessive, "torching" may result in local removal of too much inhibitor, and subsequent local mould reaction may occur even though the surface is dry, presumably by reaction with the combined moisture in the clay.<sup>29</sup> Condensation of moisture on chills must also be avoided.

Flushing large moulds with SO<sub>2</sub> immediately before filling minimizes the chance of a cold shut.

#### (d) *Other Moulding Materials*

Magnesium castings can be produced by shell moulding<sup>30</sup> and have been made experimentally in plaster moulds.

### 3. CORES

A very desirable property of cores for magnesium sand castings is that of ready collapsibility § at the pouring temperature in order to avoid hot cracks in the casting. Core sand must also contain inhibitors, and since these are volatile at the normal baking temperature, control of the baking cycle must ensure that the inhibitor content has not been reduced too greatly. The simplest core mix employed is identical with one of the moulding sands mentioned above, i.e. a washed silica sand bonded with bentonite and containing sulphur and boric acid. This mixture has the advantage that it requires no separation at the "knock out" stage and is incorporated into the moulding-sand system, thus affording a method by which new sand is added to the system. This sand is, however, comparatively weak and friable and requires a high degree of skill to permit its successful use. Sands containing linseed oil and molasses are also used, but give very hard cores. There is a growing preference for the use of urea formaldehyde resins which are well suited as core binders for magnesium.|| CO<sub>2</sub> process cores ¶ are valuable for dimensional accuracy and ready collapsibility. Shell-moulded cores are also used. Current American core practice has been recently described.<sup>22</sup>

Control of core preparation should follow the conventional lines of determinations of sieve analysis,

expansion of magnesium and is exemplified by a large aircraft wheel-fork casting which actually contracts 1 in. in length whilst cooling down to room temperature after pouring.

|| If urea formaldehyde resins are used, the boric acid content should not exceed about ½%, otherwise the core strength is reduced.

¶ Sulphur (1%) is used as the inhibitor. Boric acid must be absent.

\* Considerable trouble with blow holes has arisen in the past from coal dust in sand transported in railway wagons previously used for coal traffic.

† In conjunction with outcropping microporosity, this can give rise to serious flux contamination in castings (Section VI.3 and ref. (17)).

‡ The A.F.S.-type tests are commonly used.<sup>28</sup>

§ The need is accentuated by the relatively high coefficient of



permeability, hardness, collapsibility, &c., but should, for magnesium, also include control of inhibitor content and venting. Attention has already been directed to the need for avoiding overbaking with loss of inhibitor, and for the same reason extra inhibitor may have to be incorporated in sand over which much hot metal is to flow. Thus, sulphur contents up to 10% may be used in special cases. Dielectric core baking should minimize loss of inhibitors.

Proper venting of cores is most important, and an inspector authorized to break up a percentage of cores can ensure that the vents are properly located. Spiked core boxes may be used.

The use of coloured core sands enables the origin of defective cores to be traced.<sup>22</sup>

Air-conditioned rooms for storing cores<sup>22</sup> should be helpful in minimizing scrap through blows, cold shuts, &c.

#### 4. CHILLS

Cast-iron chills used for magnesium castings may be scored or vented to ensure that the metal lies smoothly against the chill. They are usually dressed by spraying with French chalk mixed with boric acid or bentonite as a bonding agent, and dried either by heating in the core-drying oven or during "torching" of the mould. An alcoholic base facilitates drying. Periodic cleaning of chills by shot-blasting or scratch-brushing should be performed.

Chills are best shaped to fit the area to be chilled, the thickness being adjusted to suit that of the casting wall.

Core-sand mixes with chilling properties are described by Chamberlin and Mezoff,<sup>31</sup> who have studied the effects of chilling on the metallurgical quality of non-zirconium alloy castings.

Mould reaction, blows, misruns, and inclusions of moulding sand are possibly the most likely results of faults in sand preparation and moulding practice. Each is recognizable without much difficulty, but with zirconium alloys local mould reaction has been detected which was not apparent by examining the surface of the casting. The effect of this reaction is to precipitate zirconium from solution, leading to local coarse grain and perhaps microporosity, even in alloys such as ZRE1 which are normally completely sound.

#### 5. RUNNING TECHNIQUES

Devising a running system for a given casting which produces consistent good quality, is economic in moulding time and metal, and gives rise to simple and cheap fettling operations is clearly a foundry matter. It may be observed, however, that the metallurgical quality of a magnesium alloy casting can be largely governed by the running technique employed. The latter must reconcile the opposing needs for clean metal to enter at the lowest part of the casting to minimize turbulence and resultant oxide inclusions, and for hot metal to be provided,

usually at the top of the casting, to ensure satisfactory feeding and soundness.\* Wherever permitted by the casting shape, an "upsprue slitgate" system† will normally give the best results.‡ In this system the metal rises in a separate vertical runner or upsprue and passes into the casting by progressive lateral flow through the slit. The latter is attached to the thickest wall of the casting and is in general thicker than the casting wall; risers are applied to thick sections near the slit and to the slit itself. A cylindrical screen in the upsprue has been used to control flow.<sup>47</sup>

Ideally, the control of running systems should include the following steps:

(i) Development of a satisfactory technique, involving inspection of castings by fracture and radiography until a satisfactory quality has been achieved.

(ii) Action to ensure that the specified technique is, in fact, employed. To a large extent this can be arranged by inclusion of runners, gates, risers, &c., on the pattern equipment or, if necessary, by having separate loose patterns for moulding the running and risering systems. Hand-cut runners and risers, though sometimes unavoidable, are obviously less susceptible to satisfactory control.

(iii) Rigorous quality checking of the first few production castings to ensure that the running technique devised produces consistent results. Some techniques are marginal in that results are inconsistent and include an abnormal proportion of rejectable castings; in such cases revision of the running system is clearly desirable.

#### 6. FOUNDRY EQUIPMENT

As with the founding of all metals, the quality of much of the equipment has a direct bearing on that of the product. Pattern equipment and moulding boxes should be kept in good condition; handling equipment for moulds, cores, and melts should operate smoothly; furnaces should be at a convenient height; § and adequate access provided for cleaning and sulphuring of melts without undue discomfort to the operators from heat and sulphurous fumes. Electric heating has advantages.<sup>32</sup>

The universal plea for better working conditions in the foundry industry indicates the need for improvement; and in an industry where quality of the product is so dependent on human skill, provision of good working conditions would seem a fundamental requirement of quality control.

#### V.—ROUTINE INSPECTION TECHNIQUES

The techniques used for the inspection of magnesium-base castings are generally similar to those for other metals, and it is intended only to point out such differences or peculiarities as deserve special emphasis.

Inspection procedures, although primarily intended to ensure that only castings of acceptable quality are despatched, should be applied so that defective material is detected at an early stage, i.e. before any unnecessary

\* This need is accentuated by the low volume heat capacity as a result of which the metal tends to flow through the mould along certain channels rather than to spread out uniformly, and also by the nucleated fine grain resulting in the "mass feeding" described by Baker.<sup>19</sup>

† Also known as a bottom-run sidegate with well or a slot gate

with vertical runner.

‡ This applies to all magnesium alloys irrespective of freezing range and whether or not they can exhibit microporosity with imperfect feeding.

§ For hand puddling zirconium alloy melts, the top of the crucible should be 18–24 in. above floor level.

processing is performed. They should be designed to permit the identification and recording of defects wherever possible, thus providing information from which the factors involved may be inferred.

The order in which the following inspection procedures are listed would be suitable for application to many cases, but appropriate modifications may be desirable for certain types of work.

### 1. PRIMARY VISUAL INSPECTION

This is normally carried out immediately after stripping the casting from the mould and serves both to eliminate useless castings and to identify those with potentially salvageable defects. Sub-surface defects such as dross, blowholes, &c., may not be visible before shot-blasting,\* so that further visual inspection after this process may be advisable.

### 2. CRACK DETECTION

This should follow fettling, heat-treatment, and any welding operations which may be required. A number of techniques are available, all of which depend on the absorption by the crack of some liquid, removal of the excess from the surface of the casting, and subsequent exudation from the crack of liquid which is identified either by colour or fluorescence. These processes will also detect any porosity that extends to the surface, the micropores acting in the same manner as cracks. None of the techniques appears completely "fool proof", but used intelligently they can be of great assistance, and their adoption is therefore becoming more general. Until recently, crack detection by visual examination of the casting was common practice, but the probability of inadequate inspection due to operational fatigue or boredom is obviously much reduced with the modern techniques.

### 3. RADIOGRAPHY

As a result of the almost complete diversion of magnesium-base structural castings to aircraft use during the war years, coupled with the demand for the highest quality in such castings, radiography has probably been applied more universally to magnesium-base castings than to those of any other metal. Radiography is indispensable in developing running methods for castings of the highest quality, although, as with all inspection techniques, it must be used intelligently and with an appreciation of its limitations.

Some castings may be of such heavy or complex section that radiography of the complete casting will not be sufficiently sensitive. In developing running techniques, such castings may be sectioned and then radiographed. With the alloys containing aluminium, radiography will not normally detect oxide inclusions unless these are very gross and contain entrapped air (i.e. "scum" inclusions), and radiography should therefore be supplemented by a break-up examination when developing running techniques.

Defects in magnesium-zirconium alloy castings are more readily revealed by radiography than is the case

with the aluminium-containing magnesium alloys, owing to the presence of radiographically dense alloying elements. Thus, oxide skins are rendered readily visible through the precipitation of radiographically dense zirconium around the skin.<sup>7</sup> Porosity in Z5Z (D.T.D. 721) is accompanied by segregation of zinc, and segregation effects in ZRE1 (D.T.D. 708) become readily apparent, since the segregating elements are zinc and the rare-earth metals. Skelly and Sunnucks<sup>34</sup> have pointed out that defects in ZRE1 which have resulted in rejection of castings would be accepted in many aluminium-base alloys because they would not normally be detectable by radiography.

Fluoroscopic techniques are not usually applied to magnesium-base castings owing to insufficient sensitivity, although this practice was used to some extent during the war as a sorting examination preparatory to radiography.

### 4. DIMENSIONAL CHECK

There appear to be no special requirements peculiar to magnesium-base alloys. The relatively high coefficient of thermal expansion ( $26 \times 10^{-6}/^{\circ}\text{C.}$ ) should, however, be borne in mind with machined parts.

### 5. FINAL VISUAL EXAMINATION

Apart from ascertaining that the casting has no obvious visual defects and that it bears its correct identification marks, &c., the final examination should ensure that the chromate treatment (usually specified for magnesium-base castings) has been satisfactorily applied and the film is dry. Pockets of moisture left in the casting could, for instance, cause corrosion damage before receipt by the customer.

Final inspection is best applied in the warehouse before despatch, where it can include checking that the method of packing is satisfactory for avoiding corrosion or mechanical damage in transit.

In addition to the above routine inspection techniques, it is advisable, and in some cases mandatory, to carry out other tests of a more specialized nature as follows.

### 6. FRACTURE EXAMINATION

Much valuable information regarding inclusions, porosity, grain-size, &c., can be obtained by examining fractured castings, and this technique should be employed to supplement radiography when developing running methods for new patterns. It may be usefully applied to castings which are scrapped in the course of manufacture. Break-up tests on a percentage basis are permitted by A.I.D. testing procedure as an alternative to radiographic inspection where the size or complexity of the casting renders radiography of doubtful value. In carrying out break-up tests on magnesium-aluminium alloys, it is customary to heat-treat for at least 2 hr. at  $300^{\circ}\text{C.}$  or above to discolour the walls of the pores, thus rendering the porosity more readily visible. It should be noted, however, that this process is satis-

\* The deleterious effect of shot-blasting on corrosion-resistance and the use of an anodizing treatment<sup>33</sup> as an alternative or a corrective measure have been dealt with elsewhere. At the time of writing, it is still common practice to shot-blast magnesium

alloy castings, although this is specifically forbidden for high-purity alloy castings supplied to D.T.D. 684 and 690, unless the entire casting surface is subsequently removed to a depth of 0.040 in.



factory only where the porosity breaks out to the surface of the casting.

## 7. PRESSURE TESTING

Pressure testing may be carried out either with water under pressure, or with compressed air, the casting being then immersed in a water tank. Castings should be dried immediately after testing. Cases have been observed where pressure-tightness has developed subsequent to or even during testing by the water method, presumably through blockage of fine pores with traces of corrosion product. It is doubtful whether such "sealing" of the casting is permanently effective, and care should be taken that the results of pressure tests are not misinterpreted owing to this effect.

## 8. EXAMINATION FOR GRAIN-SIZE

Indirect control of grain-size in melts of magnesium-base alloys is effected in the course of routine tensile testing of separately cast test-bars, since grain-size has a pronounced effect on tensile strength. The use of fracture tests on bars taken from melts before casting has already been mentioned for both zirconium- and aluminium-containing alloys.

## 9. EXAMINATION FOR FLUX CONTAMINATION

The occurrence of flux-inclusion troubles in a well-run foundry is rare, and no tests for flux are normally carried out on castings.

Visual examination of a casting reveals chloride contamination breaking out to the surface, and a more searching examination can be made by applying the technique described elsewhere<sup>17</sup> to scrap castings or to risers cut from castings. Gross chloride contamination may also be detected on fractured surfaces if these are stored for a few hours under conditions where external contamination is avoided. In all techniques for detection of chloride contamination, it is desirable to avoid contamination from external sources and essential to recognize that such contamination may show results deceptively similar to those of normal contamination (Section VI).

## 10. STATISTICAL ASPECTS OF CONTROL

Statistical control of castings quality forms the subject of a separate contribution to this Symposium.\* It may be noted, however, that whereas many aspects, such as mechanical properties of test-bars, are obviously suited to statistical control, others less readily capable of numerical assessment may be treated statistically if first assessed visually on some arbitrary scale. An example is microporosity appearing on radiographs, though Busk<sup>35</sup> has described a method for its quantitative assessment based on the "contrast index".

## VI.—THE ORIGIN AND CORRECTION OF OBSERVED DEFECTS

In this section, the aim has been to cover all the various defects which *can* arise in magnesium alloy

castings, and the list may therefore appear somewhat formidable. It should be remembered, however, that many thousands of tons of virtually perfect castings have been and are being made, and that magnesium alloy castings, in particular those for aircraft use, will stand comparison as regards quality with any others.

For the purpose of this section, it will be convenient to classify the various defects according to the tests by which their presence is disclosed.

### 1. DIMENSIONAL DEFECTS

Dimensional defects offer no special problems, magnesium alloys being stable dimensionally. Certain types of casting may require "setting" in jigs to an exact shape (Section VIII).

### 2. VISIBLE SURFACE DEFECTS

Defects such as rough surface, sinks, cold shuts, sand holes, blows, and "cope pits"† may be regarded as foundry matters lying outside the scope of the present paper.

#### (a) Mould Reaction

Although generally indicated by white oxide patches on the surface of the castings, mould reaction may occur to a detrimental extent in alloys containing zirconium without external indications being present. Metallographic examination may show outcropping "spider microporosity"‡ and, in the case of zirconium alloys, local coarse grain and zirconium precipitation. The cause is insufficient inhibitor, possibly arising through loss of sulphur from cores during baking, or from areas in contact with a large section of metal or over which a lot of hot metal flows. Accumulation of water-soluble salts in moulding sand also promotes mould reaction and can lower permeability. Mould reaction can be reduced by beryllium additions provided that the desired tensile properties can still be attained.§

#### (b) Cracks

These may be attributable to use of hard cores; an unsuitable alloy, e.g. Z5Z for a cockpit canopy framework casting; low rare-earth or high zinc contents in Mg-RE-Zn-Zr alloys; coarse grain-size due to poor grain refinement in magnesium-aluminium-type alloys, or low effective zirconium content in any of the zirconium alloys; or removal of castings from the moulds whilst still very hot.

As already indicated, various techniques for crack detection may usefully be employed to supplement visual examination.

#### (c) Blue Surface Mottling

Inverse segregation appearing as blue mottling|| (due to Mg<sub>2</sub>Si) can occur in magnesium-aluminium alloys, particularly the commercial grades. It is associated with coarse grain,<sup>36</sup> and the remedy is to avoid low pouring temperatures and rapid cooling, and to ensure adequate grain refinement. It is of little practical consequence

\* A. R. Martin, *J. Inst. Metals*, 1956-57, **85**, 209.

† Cope pits take the form of very small globular holes on the cope surface of the casting and appear to be associated with air caught in the metal stream. They are said to be more prevalent with ZK51 (Z5Z), but are practically unknown in the U.K.

‡ See ref. (17), Fig. 27 (Plate L).

§ Beryllium coarsens the grain of magnesium-aluminium-type alloys and is a partial alloying inhibitor element for zirconium.

|| Illustrated by Payne.<sup>36</sup>

except that if it is of appreciable depth, production of uniform chromate films on the castings may be difficult.

#### (d) Corrosion Spots

These may be due to flux inclusions or to some form of external contamination by chlorides, e.g. exposure to chloride-containing dust,\* placing the casting down on a surface contaminated with chloride, &c.† Examination at low magnifications will often reveal non-deliquescent particles of dust or iron-scale at the centres of spots caused by external contamination, whilst microscopic examination fails to reveal flux-associated structures in the underlying metal. No further corrosion will develop if the surface is skimmed and exposed to clean damp air.

Diagnosis of the cause of flux inclusions is generally possible from microscopic observation, as indicated in the next section.

### 3. CORROSIVE INCLUSIONS APPEARING ON EXPOSURE OF A PREPARED SURFACE TO DAMP AIR ‡

The detection, examination, and diagnosis of the origin of chloride-containing inclusions have been dealt with at some length elsewhere.<sup>17</sup> Certain precautions are necessary to avoid external contamination of the prepared surface with chloride-containing dust, and use of a humidity chamber of controlled relative humidity is desirable. Steaming of castings, though non-destructive,

TABLE II.—Principal Categories of Flux Inclusion

Microscopic Appearance (Structures in underlying metal after removal of corrosion product)	Origin of Inclusion	Remedy
Oxide skin inclusions possibly with mechanically swept up Mn-rich particles. (See ref. (17), Figs. 13-14, Plate XLVII.)	Insufficient care in cleaning metal surface before casting.	Follow suggested cleaning procedure. Check that flux cover is neither fluid nor powdery at time of pouring.
Spider microporosity. (See Ref. (17), Figs. 8-11, Plates XLV and XLVI.)	Sucking of chloride film from metal surface into out-cropping microporosity during solidification.	Check mould sand for chlorides. Degas melt (non-Zr alloys); avoid use of dirty scrap. Improve local feeding on castings. Avoid fluid flux cover at time of pouring.
Skins and microporosity absent, and few or no Zr-rich particles present.*	Pouring too fast.	Pour more slowly and smoothly from crucible. Use smaller pouring box. Reduce sprue area.
Many clusters of Zr-rich particles. (See Ref. (7), Figs. 5-9, Plates LIV and LV.)*	Too much metal poured from crucible.	Use sufficiently large crucibles and metal charge to enable proper amount of metal to be left in crucible. Check that sufficient metal actually left by casting off and weighing.

\* These apply to zirconium alloys only.

is of limited value as a test for flux, since even the salt in human perspiration can cause conspicuous corrosion spots to develop where the castings have been touched.

\* Falls of dust from roof trusses, &c., during shut-down periods or during storms or snow-falls are frequent causes of external contamination.

† See also ref. (17), Fig. 19 (Plate XLVIII).

‡ As already indicated, flux inclusions in castings are rarely encountered, and this test would be carried out only if, for some

reason, flux inclusions arising in castings fall broadly into three categories according to whether they are associated with oxide, microporosity, or metallic particles. § Unless very extensive corrosion has occurred, microscopic observation of the remains of a corrosion spot after removal of the bulk of the corrosion product will disclose the nature of a flux inclusion (Table II). Care must, however, be taken to avoid mistaking a network of residual corrosion pits for spider microporosity.

### 4. DEFECTS INDICATED BY FRACTURE TEST

The fracture test is mainly of advantage in disclosing oxide, coarse grain, and microporosity, the latter being

TABLE III.—Defects Indicated by Fracture Test

Visual Appearance of Fracture	Cause	Remedy
Black to golden specks or films. (See Ref. (17), Figs. 5-7, Plates XLIV and XLV.)	Oxide, nitride, sulphide.	Modify running and gating to minimize turbulence. Use of blind runners or skim bobs. Fill mould with SO <sub>2</sub> . Take increased care to avoid oxidation of metal stream during pouring.
Round dark spots about 1 mm. in. dia.	Sand inclusions. (Microscopic examination usually discloses grey centre with shell of brown lamellar constituent and blue Mg <sub>2</sub> Si.)	Blow loose sand away from mould surfaces. Avoid overdrying of moulds. Avoid very rapid pouring.
Faint grey patches (in Mg-Al or Mg-Mn alloys).	Mn particles or porosity. (Check microscopically.)	Do not pour from too low in crucible.
Patches of dark grey discoloration (in Mg-Zr alloys).	Zr-rich particles. (Check microscopically.)	Do not pour from too low in crucible.
Patches of dark grey discoloration in non-Zr alloys. (See Ref. (17), Fig. 5, Plate XLIV, Fig. 18, Plate XLVIII.)	Dispersed oxide attributable to very poor melting practice.	Apply sufficient flux during melting.
Yellow-brown or pinkish discoloration (especially after heat-treatment).	Microporosity.	Improve feeding. Degas melt (non-Zr alloys). Apply chills.
Coarse fracture.	Insufficient grain refinement; or presence of Zr or Be in Mg-Al alloys; or Al, Si, &c., in Mg-Zr alloys.	Increase dose of carbon inoculant and/or superheating. Transfer coarse-grained melt to separate crucible and re-treat with carbon or zirconium. Avoid contamination of melts.

much more readily detected in castings which have been heat-treated. Metallic particles, if present in local concentrations, may also be indicated. In addition to its value as a destructive test in developing running methods and as a periodic check on quality of castings in regular production, fracturing may, of course, also be applied non-destructively with advantage, e.g. to risers for an indication of grain-size and general cleanliness of the metal. Table III summarizes information obtain-

reason, flux inclusions were suspected.

§ It is to be noted that this classification, which involves some simplification, is not complete, and in particular that other types of chloride inclusion associated with zirconium-rich particles can arise in zirconium alloys if suitable alloying salts and fluxes are not used.<sup>7</sup>



able from the fracture test and indicates appropriate remedial steps.

## 5. DEFECTS INDICATED BY RADIOGRAPHY

As already indicated, radiography is valuable in disclosing porosity, oxide and metallic particles, and segregation of certain elements. Since the sensitivity varies with the section thickness, defects are seen more readily after machining, and the technique is most sensitive when applied destructively to thin sections (e.g.  $\frac{1}{4}$ -in. thick) cut from castings.

Flux *per se* is not normally visible radiographically in non-zirconium alloys, although the structures with which any flux present would be most likely to be associated, namely oxide and clusters of swept-up manganese patches, may themselves be readily visible. The same is generally true of the zirconium alloys, though since the fluxes for these alloys are rich in  $\text{BaCl}_2$ , any gross inclusions will be visible themselves in addition to associated oxide or particles.

Radiographic inspection of non-ferrous metal sand castings forms the subject of a separate paper,\* and some of the special features shown by radiographs of zirconium alloys have been indicated elsewhere.<sup>7</sup> The following points may perhaps usefully be stressed.

### (a) Oxide

Although oxide inclusions in magnesium alloys normally appear dark,<sup>†</sup> they appear light in zirconium alloys (Fig. 2 (a), Plate XLIII) because of a layer of metallic zirconium particles precipitated on the  $\text{MgO}$ .<sup>‡</sup> For this reason, radiography is an incomparably more sensitive tool for detecting oxide in zirconium alloys than it is in other magnesium alloys.

Very exceptionally, dark oxide may appear on zirconium alloy radiographs, indicating heavy oxide scum with associated voids. This has been seen only where the flux cover was removed completely before pouring and the melt was cast hot and poured very fast.

### (b) Variations in Radiographic Density

An interesting feature shown by zirconium alloys is the occasional occurrence of sharply separated contiguous areas of differing radiographic density (Fig. 2 (b), Plate XLIII), although there is no corresponding lack of homogeneity in the metal detectable by microscopy. Extensive tests, in particular by G. B. Partridge, on miniature tensile specimens taken across the junction of such areas show that there is normally no weakness, either local or general, in the metal at such points. The phenomenon is perhaps due to the presence of zirconium as a sub-microscopic precipitate in the lighter regions.

### (c) Microporosity

The unusual orientation of microporosity in zirconium alloys should be noted.§

### (d) Sand Inclusions

These appear on zirconium alloy radiographs as sharply defined round light areas (Fig. 2 (c), Plate XLIII) approaching 1 mm. in dia. and with the rim often lighter in depth than the centre.||

### (e) "White Lines"

In view of the relatively high radiographic density of rare-earth metals and thorium, any segregations of these metals in ZRE1 and ZT1 alloys are easily seen. Two types encountered are "healed hot tears" and "healed microporosity",¶ and they arise from the filling up of incipient hot tears or microporosity by  $\beta$ -rich liquid metal. Skelly and Sunnucks<sup>34</sup> have shown that these segregations have remarkably little effect on tensile, creep, or fatigue properties of the alloy. They can usually be eliminated by modifications to feeding and gating.

### (f) Particles

Because of the radiographic density of zirconium, Zr-rich particles are easily seen on radiographs of zirconium alloy castings (Fig. 2 (d), Plate XLIII). Even dense concentrations of particles such as would be obtained by pouring the dregs of a zirconium alloy melt into a mould appear to be without serious effect on the tensile and creep properties of ZRE1 castings.\*\*<sup>37</sup>

## VII.—GRAVITY DIE-CASTINGS

Magnesium alloys for gravity die-casting are usually melted in crucible-type lip-axis tilting furnaces, although bale-out furnaces are also used. The metal is melted and refined in the normal manner in the tilting furnaces, from which it is subsequently poured into hand ladles and transferred to the die. Burning in the hand ladles is prevented by application of sulphur or sulphur/boric acid mixture as in the case of sand castings. The precautions required in melting and cleaning before casting are identical with those for sand casting. Additionally, it is, of course, necessary to ensure that the casting ladles are clean and dry. Normally no dressing is used on the hand ladles, and if these are bowl-shaped and free from sharp corners they can readily be cleaned by wire-brushing or shot-blasting from time to time.

Since the metal in the tilting furnace is held at relatively low temperatures (720°–760° C.) for prolonged

\* S. Fry, *J. Inst. Metals*, 1956–57, **85**, to be published.

† This arises from the slight voids associated with skin inclusions. These latter represent the remains of old interfaces between metal and air which have penetrated the meniscus.

‡ The radiographic markings often resemble photographs of diffuse galactic nebulae.

§ Whereas the Mg–Al alloys, even when fully grain-refined, resemble the Al–10% Mg alloy D.T.D. 300A in exhibiting "layer porosity" arranged at right angles to the direction of the temperature gradient, the Mg–Zr alloys show "ribbon" or "whirl porosity" distributed in a manner differing from that in other non-ferrous alloys. Thus, with a round bar cast upright the porosity will tend to be in horizontal layers in Mg–Al alloys, but in vertical concentric shells in Mg–Zr alloys. In certain zirconium-

free magnesium alloys of high zinc content where it is possible to effect pronounced grain refinement with iron, similar "whirl" porosity has been noticed. The phenomenon may therefore be associated with extremely fine grain produced by a nucleation mechanism, and it may be possible to induce it in Mg–Al alloys if more effective grain-refining agents can be found.

|| For microscopic appearance of sand inclusions, see ref. (7), Fig. 33 (Plate LXI).

¶ Both types are illustrated in ref. (34).

\*\* In wrought alloys, the presence of clusters of zirconium particles may cause trouble in forging, as is also the case with manganese particles. Methods have therefore been developed for controlling the incidence of such particles in wrought stock.

periods, the aluminium-containing alloys will tend to grain coarsen, and periodic checks of grain-size should be made (e.g. by examining the fracture of a suitable sample). If necessary, the alloy can be grain refined again, and the use of the carbon inoculation process is most convenient for this.\* Care must be taken to keep the flux cover in good condition throughout the pour, and if this becomes dry and brittle it should be removed and replaced with fresh flux.

Bale-out furnaces, in which the metal may be held under a relatively fluid "self-sealing" flux cover, are used to some extent and the main precaution required is to avoid flux inclusions in the castings. This demands rather more skill on the part of the operator than is the case with tilting furnaces, and more rigorous inspection of the castings for flux.

Bale-out furnaces, in which the metal is held under a dome filled with  $\text{SO}_2$ , are also used.<sup>22</sup> In this case, the metal is usually melted in a separate furnace, using normal fluxing procedures, and transferred in the molten state to the bale-out furnace. In practice, it proves impossible to suppress oxidation completely when using an  $\text{SO}_2$  cover, and in the absence of flux a gradual build-up of oxide occurs. Periodic fracture tests of sample bars or actual castings are therefore required to ensure that the metal remains substantially free from oxide. The latter may be removed by periodic fluxing with a heavy non-wetting flux, e.g. Dow No. 220,<sup>1</sup> and subsequent removal of the flux residue from the crucible by sludging. With this procedure, careful inspection of the castings for flux inclusions should be made.

With all types of furnaces, it may be preferred to add a small amount of calcium (e.g. 0.02–0.10%) to the aluminium-containing alloys to reduce the tendency of the metal to oxidize. If this procedure is followed, the quantity of calcium added must be controlled, since an excess will lead to embrittlement in the cast state and will modify the thermal cycle required for correct solution-treatment.<sup>38</sup> Beryllium is more effective than calcium in suppressing oxidation, but the addition must be restricted owing to its grain-coarsening effect with resultant reduction in mechanical properties. A nominal addition of 0.001%<sup>39</sup> made via an aluminium–5% beryllium hardener alloy is suitable.

The production of gravity die-castings in the zirconium alloys is relatively new and appears to be confined to the lip-axis tilting type of furnace. The melting and alloying procedures are similar to those for sand castings, but, as is the case with the aluminium-containing alloys, some grain coarsening may occur on holding for prolonged periods due to precipitation of dissolved zirconium. The zirconium content can be replenished during the course of the pour by re-puddling the melt. With both the aluminium- and zirconium-containing alloys, it is a wise precaution to adapt the size of melt to the casting rate so that individual melts are not held for excessively long periods.

The production of sound gravity die-castings depends on correct die design, operating temperature, die dressing, metal temperature, method of filling the mould, and method of stripping. Many of these factors are inter-

connected, and much of the operation of die preparation and casting depends on the skill of the individual operator. Rough inspection of the castings takes place immediately on production, so that suitable modifications of procedure may be made promptly to correct any defects.

Further inspection follows similar lines to those already indicated for sand castings, rather greater emphasis being required on crack detection owing to the higher probability of the occurrence of this defect in die-castings.

## VIII.—HEAT-TREATMENT, STRESS-RELIEF, SURFACE PROTECTION, &c.

The processes of heat-treatment, stress-relief, and surface protection of magnesium castings concern the present paper only in so far as their application may affect the metallurgical quality of the product.

### 1. HEAT-TREATMENT

Control of heat-treatment provides few special features. A protective atmosphere containing 1%  $\text{SO}_2$  is desirable for temperatures above about 350° C.

Accidental surface contamination with aluminium or zinc must be avoided at these temperatures, since this can give rise to local melting with subsequent oxidation or even ignition of castings. Jigging is not normally required, but reasonable care should be taken in stacking the castings in the furnace to minimize risk of distortion.

The efficiency of solution-treatment of A8-type alloys is reflected in the tensile properties of test-bars treated with the castings. If the latter are not satisfactory, microscopic examination of the test-bar corpses will show if inadequate solution or fusion<sup>40</sup> have occurred. A stepped solution-treatment is desirable with A8 and AZ91 to obviate incipient fusion, leading to a type of microporosity.<sup>40</sup> It also minimizes grain growth ("germination"), to which the American alloy AZ92 is somewhat prone.<sup>41</sup>

### 2. STRESS-RELIEF

Since stress-relief is effected by heating to temperatures at which creep can occur, the residual stress left in the casting depending on the creep-resistance of the alloy at the temperature employed, the problem of controlling internal stress is reduced to one of specifying appropriate heat-treatment cycles and ensuring that these are properly applied. Valuable work on suitable thermal cycles for stress-relieving magnesium alloy castings has been done by Payne.<sup>42</sup>

Where either solution- or full heat-treatment is applied to magnesium–aluminium alloys, effective stress-relief is automatically obtained. Otherwise stress-relief in these castings can be readily achieved with a 2-hr. treatment at 330° C.† The same treatment suffices for Z5Z, and if combined with a subsequent period at 180° C. (e.g. 16 hr.), better tensile properties are obtained than with a precipitation-treatment at 180° C. alone.

\* If satisfactory grain refinement is not maintained, objectionable inverse segregation may arise, leading to difficulties in subsequent chromating of the castings.

† This is the highest temperature possible if solution of  $\text{Mg}_2\text{Al}_3$  is to be avoided.



The creep-resistant alloys ZRE1 and MCZ can usefully be stabilized by heat-treatment at the expected operating temperature of 200°–250° C. Payne has confirmed that treatment for 10 hr. at 250° C. effects some stress-relief of MCZ and is without adverse effect on creep properties at 200° C.\* or tensile properties at room temperature. Where required, full stress-relief of MCZ without damage to creep properties can be obtained by solution-treatment at 565° C. This may sometimes involve the use of jigs to avoid distortion.

ZT1 is normally given a 16-hr. heat-treatment at 315° C. (600° F.), and this is believed to effect a useful degree of stress-relief.

### 3. "SETTING" TO PARTICULAR DIMENSIONS

If it is desired to "set" castings, e.g. door- or window-frames, to exact shapes without giving rise to internal stress, this can be done by use of jigs and temperatures suitable for stress-relief. Thus the magnesium-aluminium alloys can be set during solution-treatment at 415° C., and Z5Z using 2 hr. at 330° C.

### 4. SURFACE PROTECTION

Surface sealing with epoxy resins, which constitutes part of the best protective treatment at present available for magnesium alloys,<sup>33</sup> involves stoving at 220° C. Tests have shown that no appreciable damage is done to the tensile properties of A8 alloy, either as-cast or solution-treated, under these conditions. RZ5, Z5Z, ZRE1, and MCZ alloys are naturally unaffected by quite long exposures to 220° C., since this is a permissible heat-treatment temperature for each.

### 5. SALVAGING DEFECTIVE CASTINGS

This subject falls outside the scope of the paper, but it may be mentioned that all the alloys appearing in Table I can be satisfactorily welded by the Argonarc process with the single exception of Z5Z. Gas welding is confined to alloys not containing zirconium, and elaborate cleaning of the weld is necessary to avoid subsequent corrosion through welding-flux entrapment.

## IX.—STANDARD OF QUALITY IN CASTINGS

No consideration of the control of quality seems complete without some reference to the standard to be achieved, to the practical effects of various defects, and to the level of properties obtainable in different parts of castings.

### 1. QUALITY REQUIRED IN CASTINGS

It has been said that the perfect casting has yet to be made and, even if a consideration of perfection is limited to factors affecting strength, this is still true. All

castings contain potentially weakening defects, and makers and users are faced with the problem of assessing the level of defects that can be tolerated.

In practice, this assessment is made by agreement between producer and consumer, guided to some extent by guesswork; and even with a highly stressed casting, the decision whether or not to accept is often a matter of opinion. The natural tendency in such conditions is to reject when in doubt, so that if either producer or consumer lacks the necessary experience there will be a risk of all castings showing defects being rejected and thus of setting an impossibly high standard for the foundry. It may be wondered how many potentially satisfactory castings have been rejected through lack of reliable information on the effect of some defect present.

Unfortunately, it is difficult to provide factual evidence suitable for general application of the effects of defects, since different types of castings are designed to withstand various combinations of stresses. A few papers, however, provide useful guidance in certain respects. Thus, Found<sup>43,44</sup> showed that sub-surface microporosity and other internal defects have relatively little effect on fatigue life, whereas surface condition and design are vital factors. Skelly and Sunnucks,<sup>34</sup> who studied the local effects of healed tears or shrinkage segregations on the tensile and creep properties of ZRE1, concluded they were without material effect. Data by K. E. Nelson<sup>37</sup> show that even densely packed zirconium-particle clusters are also without serious effect on the creep and tensile properties of ZRE1. In fact, Nelson expresses the view that otherwise acceptable castings should not be rejected on account of the presence of healed tear or shrinkage segregations, or of zirconium particles.† No data appear to have been published on the mechanical consequences of the sudden variations of radiographic density that can occur in zirconium alloys, but unpublished work, supported by general experience, indicates that they are not accompanied by any weakening effect. Busk<sup>35</sup> has studied the assessment of microporosity in magnesium-aluminium alloys and correlation of the results with tensile and fatigue data.

On many other aspects of the problem, less information is available. The strengths of actual castings provide an example, test-bars cut from the castings giving little information on this subject and mainly serving as a check on metal quality, for which purpose a standard test-bar separately cast under controlled conditions is preferable. In some alloys, the effect of an oxide inclusion on tensile strength depends on its location in the test specimen, a small outcropping skin being more damaging than a large inclusion entirely within the test section. The relation between microporosity in the zirconium alloy Z5Z and tensile properties does not appear to have received much study, but it must differ from that found by Busk for magnesium-aluminium alloys, since underfired Z5Z with very appreciable microporosity can still show full tensile properties. This is no doubt attributable to the tendency for any microporosity

\* It may be noted in this connection that creep properties published by Magnesium Elektron, Ltd., on these alloys relate to the stabilized state, since they were determined after 24 hr. prior soaking at the testing temperature.

† The present authors, however, would be inclined to reject

castings showing considerable areas of densely packed zirconium particles, indicative of metal from the bottom of a melt, since this is rendered somewhat viscous by the particles and readily entraps small amounts of flux.

in Z5Z to lie parallel to the major casting axis (Section VI 5 (c)); test specimens cut transversely to this axis might show a reduction in properties. Fatigue endurance of Z5Z appears to be reduced by any microporosity present, in much the same way as does that of A8.

On one aspect of quality there appears to be universal agreement; detection of cracks automatically rejects a casting. (The casting may, of course, be salvageable by welding.)

More information is desirable on the mechanical effects of defects generally, and the publication of "case histories" of tests on given castings or of research work with a specially designed test casting might serve a useful purpose.

## 2. PROPERTIES ATTAINABLE IN CASTINGS

Detailed consideration of the mechanical properties attainable in various parts of castings made by suitable running techniques and in various alloys lies outside the

TABLE IV.—*Summarized Tensile Property Data on Bars Cut from Test Casting GR 14<sup>25</sup> in Two Alloys.*

Alloy	Tensile Properties (Expressed as percentage of minimum properties of separately cast test-bars)		
	0-1% P.S.	U.T.S.	Elongation, %
A8 Solution-treated (B.S. L122)	79-108	72-126	105-310
Z5Z Heat-treated (D.T.D. 721A)	99-120	99-126	100-260

TABLE V.—*Summarized Tensile Property Data on Bars Cut from Two Large Undercarriage Castings in Meltron Z5Z.*

Position No.	Section, in.	Tensile Properties (Expressed as percentages of minimum properties of separately cast test-bars)			
		0-1% P.S.		U.T.S.	Elongation, %
1	1 $\frac{3}{4}$	94	96	84 97	75 100
2	1 $\frac{3}{4}$ (C)	99	74	93 73	100 60
3	1 (C)	82	94	93 87	100 70
4	1 (C)	82	94	96 88	120 80
5	1 (C)	85	94	100 95	160 100
6	1 $\frac{1}{4}$	87	94	91 88	100 80
7	1 $\frac{1}{4}$	82	101	105 99	200 100
8	1 $\frac{1}{2}$ (C)	82	90	68 71	25 20
9	1 (C)	87	90	81 87	80 50
10	1 (C)	87	94	84 97	80 110
11	1 (C)	85	99	89 99	80 100
12	1 $\frac{1}{2}$ (C)	96	94	87 95	60 100
13	1	96	94	92 92	100 70
14	3 × 4	96	93	89 93	90 80
15	3 × 4	87	—	108 96	170 80
16	1 $\frac{1}{2}$ (C)	92	92	103 89	170 60
17	1 $\frac{1}{2}$ × 4 (C)	89	94	108 104	240 40

(C) — Chilled.

intended scope of this paper, but the general level of tensile properties which may be obtained can be judged from data published by Ball.<sup>8</sup> These results relate to a special test casting<sup>25</sup> with varying sections and cover the

typical high-strength alloys A8 (B.S. L122) and Z5Z (D.T.D. 721A). Table IV summarizes the maximum and minimum properties found in various positions in this casting expressed as a percentage of the minimum test-bar properties given for the alloy in Table I.

It will be seen that the level of properties is particularly good in the zirconium alloy Z5Z, and this is further illustrated by tensile data on bars cut from large, thick-walled aircraft undercarriage castings (Table V). This casting weighs 439 lb. net and provides a wide range of thick sections.

For the creep-resistant alloys, K. E. Nelson<sup>26, 48, 49</sup> has shown good accordance between the properties of bars from castings and those of separately cast test-bars. The same is true of the high-strength thorium alloy, T26.<sup>50</sup>

## 3. EFFECTS OF VARIOUS FACTORS ON MECHANICAL PROPERTIES

Certain factors such as minor variations in composition or heat-treatment within the ranges permitted by the appropriate specifications, degree of chilling, &c., may have appreciable effects on the mechanical properties or corrosion-resistance of the various alloys, but it is felt that detailed discussion of this subject falls outside the scope of the present paper.

## X.—THE ORGANIZATION OF PRODUCTION TO FACILITATE THE CONTROL OF QUALITY IN MAGNESIUM ALLOY CASTINGS

The object of this section is to offer a few suggestions, based on the authors' experience, concerning arrangements which, it is thought, can contribute to the achievement and maintenance of high quality. It is clearly impossible to specify a single type of organization which would be the most suitable for all foundries, since, amongst other things, individual personalities, factory lay-out, and the type of work undertaken, all have an influence on the organization best suited to any given foundry. The following suggestions are for the most part therefore quite general, and of course their application is not necessarily restricted to magnesium alloys.

### 1. RESPONSIBILITY FOR METAL QUALITY

Close liaison must always exist between the foundry, metallurgical, and inspection staffs, but it is preferable that the metallurgical department should be responsible for the quality of metal entering the casting. A furnace foreman, or production metallurgist with executive authority, responsible to the chief metallurgist for metal quality, appears a better arrangement than one in which the metallurgical staff act merely in an advisory capacity.

### 2. CONTROL OF INSPECTION

The chief inspector should not be held responsible to anyone directly concerned with production. Arrangements whereby the chief inspector is responsible to, or at least has ready access to, a company director are



probably most usual and permit the independence of action required to maintain quality at the highest level.

### 3. CONTROL OF DEVELOPMENT WORK

New work, including development of running systems for new patterns, investigation of new processes, &c., should be in charge of someone who has no immediate responsibilities for production. To obtain the best results from this type of work, a foundryman is required with more than average ability to plan systematic development and to assess results critically. Responsibility for this work should be vested in the foundry manager, but it is preferred that the development personnel should have no direct responsibility for production. For much work of this type, a separate development foundry is very desirable, and in the case of a fully mechanized plant, almost essential. In most jobbing foundries, however, adequate facilities can usually be provided without the need for a separate foundry.

### 4. STANDARDIZATION OF PRODUCTION TECHNIQUES

As far as possible, all production techniques should be standardized and catalogued. In particular, an adequate record should be maintained of the casting techniques for each pattern, and all changes, together with the reason for the change, carefully noted. The maintenance of such records requires a continuous and positive effort and is probably best made the responsibility of one person. For aircraft castings, this will normally be an A.I.D.-approved metallurgist, but the importance of keeping proper records for other castings should not be overlooked.

### 5. ANALYSIS OF ORIGIN OF SCRAP

Defects in castings can be grouped into a number of well-defined categories, and it should be the responsibility of the inspection department to allocate to the appropriate category all castings which it rejects. Periodically (e.g. daily or weekly) a summary of rejects, listing both pattern number and reason for rejection, should be issued, and these summaries should provide the evidence on which the success of plans to reduce the rejection rate are judged. Similarly, all complaints and rejections by customers should be catalogued and reviewed (e.g. at monthly or quarterly intervals). A quarantine store for castings rejected by customers is useful, as is also a store or bay for castings rejected from current production. The castings can then be readily examined by inspection, foundry, laboratory, and other interested personnel.

### 6. AVOIDANCE OF CONTAMINATION IN ZIRCONIUM ALLOY MELTS

Since aluminium can precipitate up to some twenty times its weight of zirconium, very little contamination with A8-type alloy will ruin a zirconium alloy melt. Encouragement of good "housekeeping" is not sufficient.

The ideal of separate foundries for alloys containing zirconium and aluminium is hardly practicable, but steps such as the following can be taken to render the likelihood of contamination very remote :

(i) Use of separate melting shops for the two classes of alloys.

(ii) Marking the risers and runners of all castings with paint indicative of the alloy, or by placing marked metal strips in riser cavities before pouring the casting.

(iii) Use of separate fettling shops.

(iv) Where (i) is not practicable, use of separate crucibles and melting tools. (These can be marked with notches indicative of the alloy). Separate hand ladles for casting test-bars are important.

### 7. COLLABORATION BETWEEN DESIGNER AND FOUNDER

Close collaboration between the founder and the customer's design staff is most desirable, so that the former can suggest and discuss modifications to design features which may be difficult or time-consuming to mould, or which may militate against the achievement of maximum soundness.\* Such collaboration is important with gravity die-castings. In fact control of quality might be said to begin with the "vetting" of customers' designs.

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# THE STABILITY OF MECHANICAL PROPERTIES OF BETA-PHASE MAGNESIUM-LITHIUM ALLOYS\*

1747

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## SYNOPSIS

It has been shown (*J. Inst. Metals*, 1955-56, **84**, 364) that when aluminium, zinc, or cadmium is added to binary magnesium-lithium alloys, good mechanical properties in the cast and rolled conditions are obtained which compare very favourably with those of other light alloys having a higher density. These alloys, however, suffer from the great disadvantage that their mechanical properties are not stable at ordinary temperatures. Attempts have now been made to decrease this instability by adding varying amounts of silver, copper, cadmium, aluminium, tin, antimony, or nickel to three basic  $\beta$ -phase ternary alloys.

The results suggest that the instability of mechanical properties may be connected with electron concentration. Lowering the electron concentration by suitable additions, or by increasing the lithium content, decreased the instability. Silver (univalent) proved to be the most effective addition. Raising the electron concentration by the addition of antimony increased the instability. Microscopic and X-ray examination showed the influence of an alteration of the electron concentration on the existence of phases which affect the stability of mechanical properties. Even though alloys containing silver or copper are not permanently stable above 16° C., the mechanical properties after ageing for 200 hr. at 75° C. are nevertheless encouraging.

## I.—INTRODUCTION

PREVIOUS work<sup>1</sup> has shown that the mechanical properties of magnesium-lithium alloys are good for alloys of such low density, and that the  $\beta$ -phase alloys (containing about 12% lithium), which have a cubic crystal structure, are very easily forged. A third metal was added to the  $\beta$ -phase alloys with the object of improving their strength and work-hardening properties without too great a sacrifice of other properties such as ductility. While good optimum properties in the cast and rolled conditions were obtained with the ternary alloys containing cadmium, zinc, or aluminium, these properties are not stable at ordinary temperatures. Alloys containing silver, copper, tin, or cerium (or Mischmetall) comprised a second group, which are stable at ordinary temperatures, but whose mechanical properties, although generally better than those of the binary alloys, are not as good as in the first group.

The present paper describes attempts to increase the stability of alloys of the first group by further alloying. Little information was available regarding the mechanism of ageing or the factors affecting diffusion in complex alloys, so that no forecast could be made on theoretical grounds as to the effect on stability of the addition of a fourth metal. However, it was to be expected that a metal which produced stable ternary alloys, i.e. one from the second group, would have a beneficial effect when introduced into ternary alloys of the first group.

After a preliminary survey, it was decided to carry out experiments on three series of  $\beta$ -phase magnesium-

lithium ternary alloys containing: (a) 7½% zinc, (b) 18% cadmium, and (c) 9% cadmium, respectively. Ternary alloys containing 7½% zinc or 18% cadmium had proved to be the strongest but the most unstable, the former having the lower density; the 9% cadmium alloy was less strong and contained just sufficient cadmium to render the alloy unstable. In the exploratory work, instability of mechanical properties was indicated by a fall in hardness values on ageing curves.

## II.—PREPARATION OF ALLOYS

The melting and casting procedure used in the earlier work was followed, except that all melts were teemed at 150° C. above the melting point.§ Ingots were removed from the moulds after 10 min. Quaternary alloys were prepared either (i) by melting the previously made basic ternary alloy and adding the fourth metal in the virgin form, or (ii) by melting the four metals in one operation (including the presolidification). Chemical analysis showed little, if any, segregation in the ingots. The latter, which were about 1 in. thick, after being scalped were heated at 400° C. for 1 hr. and hot rolled to 10 S.W.G. in 9 passes. In addition to British Standard tensile test-pieces cut longitudinally from the sheets, small specimens (½ in. square) were made for hardness determinations, which were carried out on a Rockwell machine ("E" scale)|| To avoid any effects due to repeated heating and cooling during ageing, each set of hardness determinations for any particular time or temperature of ageing was made on separate pieces, an

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§ Alloys which contained antimony were teemed at 950° C., owing to the possible presence of compounds having a high melt-

ing point.

|| This machine was used instead of the more usual Vickers machine for convenience and speed; the two machines gave similar results.

ageing curve requiring about 30 specimens. Specimens were held at 450° C. for 4 hr. in argon, quenched in water at room temperature, and then aged in temperature-controlled air ovens or kept in a room which varied very

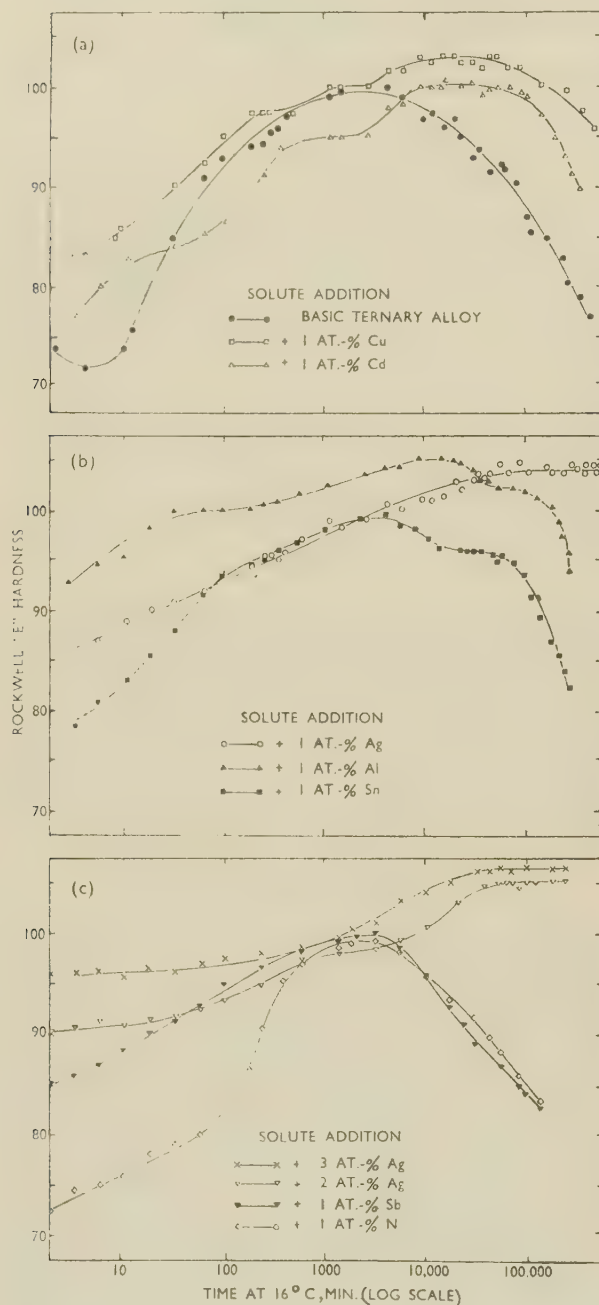


FIG. 1 (a)-(c).—Ageing Curves at 16° C. for Quaternary Alloys. Basic ternary composition Mg : Li = 88 : 12, Zn 7½%.

little in temperature. Ageing curves were drawn for 16°, 50°, 75°, and 100° C. and those for 16° and 75° C. are reproduced in Figs. 1-4. Silver produced the greatest effect, stabilizing the three basic ternary alloys at ordinary temperature and decreasing the instability

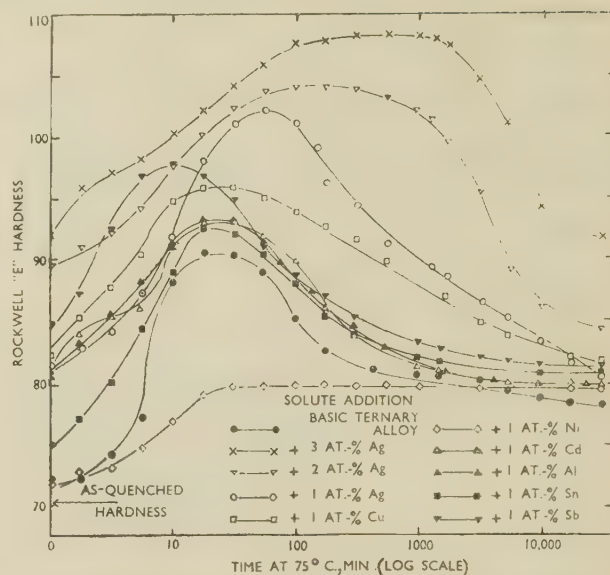


FIG. 2.—Ageing Curves at 75° C. for Quaternary Alloys. Basic ternary composition Mg : Li = 88 : 12, Zn 7½%.

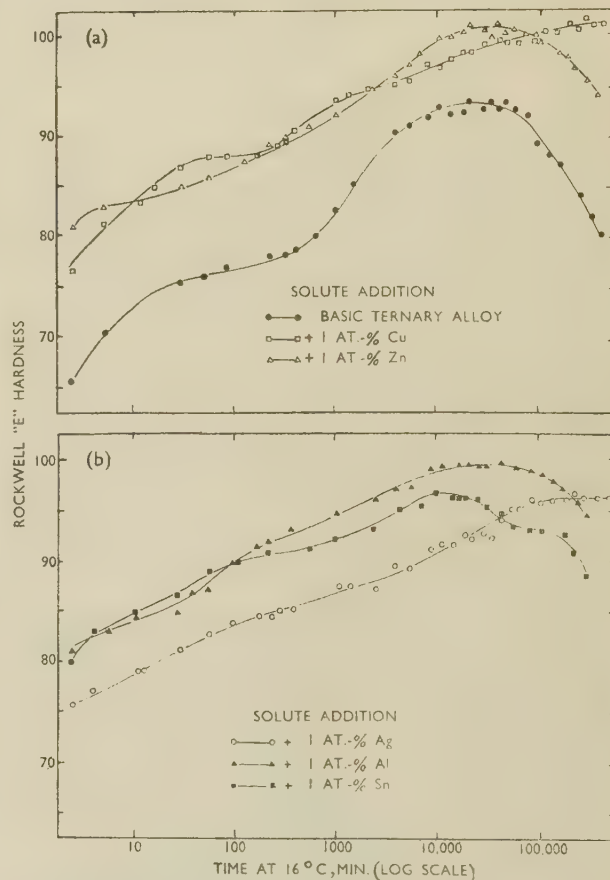


FIG. 3 (a) and (b).—Ageing Curves at 16° C. for Quaternary Alloys. Basic ternary composition Mg : Li = 88 : 12, Cd 18%.

at higher ageing temperatures. Copper, zinc,\* cadmium,\* and aluminium reduced instability, whereas tin had little effect.

\* Zinc added to basic ternary cadmium alloy, and vice versa.



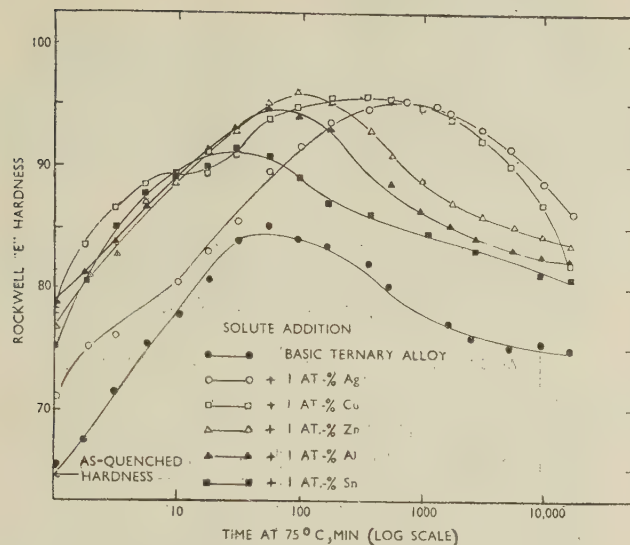


Fig. 4.—Ageing Curves at 75° C. for Quaternary Alloys. Basic ternary composition Mg : Li = 88 : 12, Cd 18%.

### III.—VALENCY EFFECT

From a comparison of the degrees of instability due to the addition of the various elements, it would appear that instability is related in some way to the valency of the solute (i.e. the fourth) element. This feature was evident in the three basic alloys at all ageing temperatures studied. The distinction between the various fourth-metal additions is more noticeable if the "effective valency" rather than the "chemical valency" is considered. The so-called effective valencies (quoted in Table I) are those given by Busk<sup>2</sup> for elements soluble in pure magnesium. They are relative values based on indium having an effective valency of 3. Busk states that the effective valencies determined from the binary magnesium alloys are applicable also to ternary alloys, provided that the (hexagonal) structure is preserved. Whether or not the same relative values hold in the ternary or quaternary alloys is open to doubt, in as much as the crystal structure is altered by the lithium addition. It might be argued that as valency is a factor of some importance in determining the extent of solid solubility of one metal in another, stability may be dependent on this solubility. This is not necessarily true, however, particularly in the case of copper, which, next to silver, was the most effective addition and which has a limited solubility in magnesium-lithium alloys. The addition of a fourth metal alters the electron concentration, and it appears that the smaller the  $e/a$  ratio, the less is the instability. The results of the present experiments support this conclusion.

Additional experiments were made to check the connection between stability and electron concentration. Alloys based on the ternary alloy containing 7½% zinc were cast which contained 2 at.-% silver (S.27), 3 at.-% silver (S.28), 1 at.-% antimony (S.29), and 1 at.-% nickel (S.25), respectively. S.27 and S.28 have a reduced  $e/a$  ratio, and it was expected that stability would be increased. S.29 has a higher  $e/a$  ratio and the stability should be lessened. Nickel is a transition element having two electrons missing in the 3d orbitals, but two

valency electrons in the outermost 4s orbital. If, in the formation of the alloys, the electrons have to satisfy the specific-energy requirements of the system, a state of affairs may be envisaged in which the nickel makes no effective contribution to the electron concentration of the alloy and thus functions as a metal with zero valency. In these circumstances the decrease in the  $e/a$  ratio would be greater than that obtained with the other metals added (silver and antimony), and minimum instability would be expected. The curves in Fig. 1 (c) and Fig. 2 show that reducing the electron concentration by larger additions of silver improved stability, but increasing the electron concentration by the addition of antimony, decreased stability. Nickel, however, did not produce the result expected, and it may be assumed therefore that the effective valency of nickel in magnesium-lithium alloys is not zero; in fact, it behaves similarly to antimony, which has a chemical valency of 5.

Table I shows the influence of the valency of the fourth metal on the instability of the alloy. In view of the difficulty in determining the time on the ageing curve at which hardness values start to fall, the time for the hardness to decrease by 5% of the maximum value has been taken as a measure of instability.

TABLE I.—The Effect of a Fourth Metal on the Instability of the Mg-Li-Base Ternary Alloys.

Addition, at.-%	Valency of Added Metal	Time (hr.) at Ageing Temperature Indicated for 5% Decrease in Maximum Hardness									
		Ternary Alloy with 7½% Zn					Ternary Alloy with 18% Cd			Ternary Alloy with 9% Cd	
		C*	E†	16° C.	50° C.	75° C.	16° C.	50° C.	75° C.	16° C.	50° C.
Ternary alloy				480	5	1½	2400	56	5	1700	320
3 Ag	1	0.66	S†	...	72	...	...	...	...	...	...
2 Ag	1	0.66	S†	...	30	...	...	...	...	...	...
1 Ag	1	0.66	S†	192	4½	S†	3100	144	S†	2400	...
1 Cu	1	1	4800	96	3½	S†	1400	96	S†	1200	...
1 Zn	2	...	...	...	4800	130	10	3500	100	...	...
1 Cd	2	2	3600	72	2	...	...	...	...	...	...
1 Al	3	2.49	2600	56	1½	4300	70	6	3100	...	...
1 Sn	4	3.5	1400	20	1½	2200	50	4	1700	...	...
1 Sb	5	...	168	4	...	...	...	...	...	...	...
1 Ni	2	0	240	...	...	...	...	...	...	...	...

\* C = Normal chemical valency. † E = Effective valency (Busk<sup>2</sup>).  
‡ S = Alloy stable for at least 6 months.

The ageing curves and the results quoted in Table I show a connection between stability and valency or, more correctly, the  $e/a$  ratio of the alloy. In these cases the  $e/a$  ratio has been lowered to decrease instability by the addition of a suitable metal. The  $e/a$  ratio could be lowered also, and stability probably increased, by raising the lithium content of the alloy. Jackson *et al.*<sup>3</sup> have confirmed that this assumption is correct and that an increase in the lithium content above that required to ensure a wholly  $\beta$ -phase structure decreased instability, the least instability was obtained with a magnesium : lithium ratio of 6 : 1.

Although improvements were effected, it was only at 16° C. that complete stability was achieved. No alloy maintained its hardness for more than 24 hr. on ageing at either 50° or 75° C. Alloys with cadmium were less unstable than those containing zinc, but unfortunately the cadmium-bearing alloys have certain disadvantages; they are heavier and undergo a phase transformation

between 75° and 100° C. The greater the cadmium content, the higher is this transformation temperature, and at higher ageing temperatures the cadmium alloys begin to soften at once. Even though the alloys were not stable on ageing at 75° C., it was considered that some of them would have a commercial use if they possessed reasonable mechanical properties after ageing for 200 hr. at 75° C.

#### IV.—PROPERTIES OF ROLLED QUATERNARY ALLOYS

Mechanical tests were carried out on alloys: (a) hot rolled and aged 3 months at 16° C., (b) hot rolled and aged 200 hr. at 75° C., (c) solution-treated at 450° C. and aged at 75° C. to maximum hardness (determined from ageing curves), and (d) solution-treated at 450° C. and aged 200 hr. at 75° C. The results are given in Tables II and III. The results on sheets tested as soon as convenient after rolling were in general so erratic, owing to the different rates of ageing, that they have not been included.

TABLE II.—Mechanical Properties of Quaternary Alloys Hot Rolled to 10 S.W.G.

Fourth Metal, at.-%	Density, g./c.c.	Aged 3 Months at 16° C.				Aged 200 Hr. at 75° C.			
		L.P., tons/in. <sup>2</sup>	0.1% P.S., tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	Elong. on 2 in., %	L.P., tons/in. <sup>2</sup>	0.1% P.S., tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	Elong. on 2 in., %
Basic Alloy Mg: Li = 88: 12 + 7½% Zn									
...	1.56	4	6	13	24	3	4½	12	40
3 Ag	1.80	10	13	18½	30	7	9½	16½	25
2 Ag	1.73	7½	11½	17½	25	5	8½	15½	20
1 Ag	1.63	6	10	16½	30	4½	7½	14½	40
1 Cu	1.60	6	9	13	33	3½	5½	12½	40
1 Cd	1.60	6	9	15½	25	3½	6	14½	32
1 Al	1.55	4½	7½	13½	35	2½	5½	12½	40
1 Sn	1.61	5	8	12½	32	3½	5½	12½	35
1 Ni	1.62	4½	7½	11½	35	2½	5½	11½	39
Basic Alloy Mg: Li = 88: 12 + 18% Cd									
...	1.73	4½	9	14½	30	3½	6	3½	35
1 Ag	1.81	7½	12½	21½	10	4½	7½	17	30
1 Cu	1.77	6½	10½	18½	20	3½	6½	15½	26
1 Zn	1.76	5½	9½	16	25	3½	6½	15½	25
1 Al	1.73	5	7½	14	42	3	6	14	28
1 Sn	1.79	5	8½	14½	20	4	7	14	20
Basic Alloy Mg: Li = 88: 12 + 9% Cd									
...	1.57	5½	8	12	35	3	5	11½	30
1 Ag	1.65	7	11½	19½	4	3	5	13	26
1 Cu	1.61	6	8½	15½	19	3	5½	11½	25
1 Zn	1.68	6	8½	15	12	4½	6½	13½	19
1 Al	1.58	4½	7	13	15	3½	6	12½	30
1 Sn	1.63	5	7	12½	15	3½	5½	11½	25

The results in Table III are disappointing, particularly as regards the alloys containing zinc. The alloys tested were chiefly those which had given stable hardness values at 16° C. and, having a relatively high hardness, might be expected to possess good tensile properties. They were extremely brittle and many specimens cracked during ageing. Microscopic examination of an alloy containing 2 at.-% silver, quenched in water after solution-treatment at 450° C. and then aged to maximum hardness at 75° C., showed the grains of the  $\beta$  solid solution surrounded by a continuous film of precipitate (Fig. 6, Plate XLIV). The alloy was still brittle after ageing at 75° C. for 200 hr. and had poor mechanical properties. To prevent formation of the grain-boundary

film and resulting brittleness, while retaining a possible improvement expected from ageing, several alloys after quenching from the solution-treatment temperature of 450° C. were cold rolled immediately to maximum hardness, in the hope that rolling would break up the films as they formed. In a further attempt to improve mechanical properties, the alloys were cold rolled (in 6

TABLE III.—Mechanical Properties of Quaternary Alloys Hot Rolled to 10 S.W.G., Solution-Treated at 450° C., Quenched in Water, and Aged at 75° C.

Fourth Metal, at.-%	Aged to Maximum Hardness				Aged 200 Hr.			
	L.P., tons/in. <sup>2</sup>	0.1% P.S., tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	Elong. on 2 in., %	L.P., tons/in. <sup>2</sup>	0.1% P.S., tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	Elong. on 2 in., %
<i>Basic Alloy Mg: Li = 88:12 + 7½% Zn</i>								
...	8½	12	16½	4	...	...	...	...
3 Ag	*	*	*	*	6½	11½	12	3
2 Ag	*	*	*	*	6½	10½	13½	4
1 Ag	8½	13	20½	0.5	7½	10½	15½	9
1 Cu	15½	17½	1½	7½	11½	11½	15½	10
<i>Basic Alloy Mg: Li = 88:12 + 18% Cd</i>								
1 Ag	8	11½	22½	5	4½	7½	16½	20
1 Cu	9½	13½	21½	10	3½	6½	15½	25

\* = Values not obtainable; specimens mostly broke in the elastic range.

passes) to 16 S.W.G. after hot rolling to 10 S.W.G. The results, given in Table IV, show that the special rolling procedure did not improve the alloys containing zinc, but it did improve those containing cadmium; the latter, however, were not originally as brittle, i.e. they did not exhibit a continuous precipitate around the grain boundaries.

TABLE IV.—Mechanical Properties of Quaternary Alloys Hot Rolled to 10 S.W.G.

Fourth Metal, at.-%	Water-Quenched from 450° C. and Rolled to Maximum Hardness				Cold Rolled to 16 S.W.G.			
	L.P., tons/in. <sup>2</sup>	0.1% P.S., tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	Elong. on 2 in., %	L.P., tons/in. <sup>2</sup>	0.1% P.S., tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	Elong. on 2 in., %
<i>Basic Alloy Mg: Li = 88:12 + 7½% Zn</i>								
...	14	19	23	2½	3½	10	15	30
3 Ag	*	*	*	*	9	14	20½	9
2 Ag	*	*	*	*	6½	12½	19	9
1 Ag	18½	*	*	*	9	12	17½	33
<i>Basic Alloy Mg: Li = 88:12 + 18% Cd</i>								
1 Ag	12½	16½	22	7	8	13	21½	5
1 Cu	14½	18½	24	10	8½	12	19½	10

\* = Values not obtainable; specimens broke in elastic range.

The mechanical properties of alloys containing zinc are reasonably good, but heat-treatment was of little benefit because of the brittleness introduced during ageing. The 18% cadmium alloys containing silver or copper were improved by heat-treatment, which produced good strength with moderately good elongation values. The properties were stable at ordinary temperature, no difference being found between test-pieces tested immediately or 6 months after the special rolling treatment.



## V.—METALLOGRAPHIC AND X-RAY STUDIES

Jackson and his co-workers<sup>3</sup> have stated that hardening in the ternary alloys is caused by the precipitation of a phase designated  $\theta$  to which they gave the formula  $\text{MgLi}_2\text{LiX}$ , where  $X$  may be cadmium, aluminium, zinc, or silver. It was inferred that the  $\theta$  phase is a transitional structure which moves towards equilibrium as ageing proceeds. Its lattice parameter had been observed to decrease during ageing (this has been confirmed), and Weinberg *et al.*<sup>5</sup> have suggested that this is caused by a change in composition of the phase brought about by the rejection of lithium atoms.

A study has been made of the structural changes occurring in a ternary  $\beta$ -phase magnesium-lithium alloy containing 7½% zinc, and also in a quaternary alloy containing silver. Diffraction patterns were obtained by rotating etched sliver specimens, using a 19-cm. camera with filtered Cu radiation, some of which are reproduced in Fig. 16 (Plate XLV). X-ray photographs of the ternary 7½% zinc alloy after quenching in water from 450° C. and ageing at 16°, 50°, and 75° C., respectively, showed the mechanism to be the same for each ageing temperature. Immediately after water-quenching from the solution-treatment temperature (450° C.), the alloy consisted of a single phase, the b.c.c.  $\beta$  solid solution. Just before maximum hardness was reached, the first diffuse reflections belonging to the precipitating phase were observed on the diffraction patterns, as shown below:

Temp., °C.	Time to Attain Max. Hardness	Time for Appearance of Reflections
75	20 min.	10 min.
50	25 "	15 "
16	60 hr.	~24 hr.

At maximum hardness, sufficient reflections were obtained to enable this phase to be identified as f.c.c. At this stage of ageing the reflections both from the matrix and from the precipitate were broad and diffuse. After maximum hardness had been passed, the diffraction pattern of the f.c.c. phase was complete, and the  $K_\alpha$  doublets of this phase and the matrix were resolvable. The f.c.c. phase appears to have a  $B32$  ( $\text{NaTi}$ )-type structure and is presumably the  $\theta$  phase identified by Jackson<sup>3</sup> as  $\text{MgLi}_2\text{Zn}$ . With the emergence of  $\theta$  as a separate phase, further reflections appeared on the diffraction patterns, belonging to the  $\alpha$  hexagonal phase. As the hexagonal phase was associated with the appearance of the  $\theta$  phase (f.c.c.), it is probable that the formation of  $\theta$  resulted in a removal of lithium from the adjacent matrix, so that the  $\text{Mg} : \text{Li}$  ratio in these areas moved to the left of the  $(\alpha + \beta)/\beta$  phase boundary in the equilibrium diagram and the  $\alpha$  hexagonal phase appeared. Observations made during the ageing of the 7½% zinc alloy at 75° C. indicated that changes in the lattice parameter of both the  $\beta$  solid solution and the  $\theta$  phase had occurred. The lattice parameter of the  $\beta$  solid solution (b.c.c.) increased from the as-quenched value of 3.5017 to 3.5168 Å. in 100 min. at 75° C., whilst further ageing for 3 weeks at this temperature increased the value to 3.5180 Å., the same as that found in the slowly cooled alloys. The lattice parameter of the  $\theta$  phase decreased during ageing at 75° C. from a maximum of 6.7000 to 6.6727 Å. in 3 weeks. The lowest value observed for  $\theta$  was 6.6660 Å., found in the slowly cooled alloy. The changes in lattice parameter during ageing

at 75° C., together with the hardness curve for the alloy, are given in Fig. 5, which shows that as soon as  $\theta$  made its appearance the hardness values decreased and the alloy became unstable. Moreover, the inflection in the lattice-parameter curve of the  $\beta$  solid solution occurs at the same ageing time.

Annealing the 7½% zinc alloy for 4 hr. at 450° C. and furnace-cooling produced a diffraction pattern showing the presence of four phases: (i) b.c.c.,  $\beta$  solid solution,  $a = 3.5180$  Å.; (ii) f.c.c.,  $\theta$  phase, ( $B32$ -type) ( $\text{MgLi}_2\text{Zn}$ ),  $a = 6.6660$  Å.; (iii) f.c.c., ( $\text{MgLiZn}$ ) phase,  $a = 7.4390$  Å.; (iv) hexagonal,  $\alpha$  phase,  $a = 3.191$ ,  $c = 5.113$  Å.

Because of the presence of the hexagonal  $\alpha$  phase, it was assumed that the alloy was not in equilibrium. Subsequent experiments involving slower rates of cooling supported this assumption, as the amounts of both  $\alpha$  and

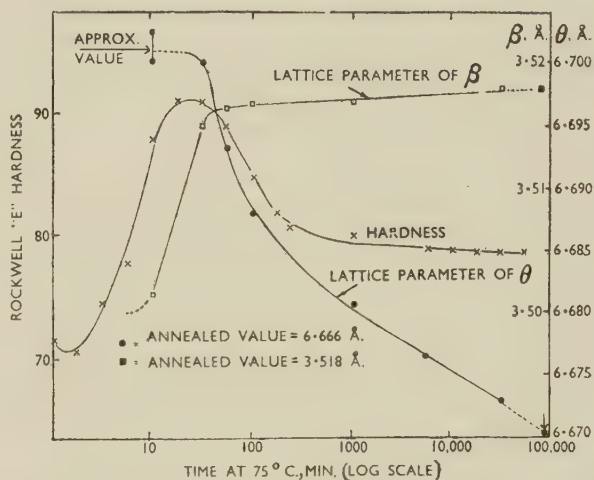


Fig. 5.—Variation in Lattice Parameter of  $\theta$  Phase and  $\beta$  Solid Solution During Ageing at 75° C. in an Alloy of Composition  $\text{Mg} : \text{Li} = 88 : 12$ ,  $\text{Zn } 7\frac{1}{2}\%$ .

$\theta$  decreased, while the amount of the second f.c.c. phase increased. The second f.c.c. phase is presumably  $\text{MgLiZn}$ , which Busk *et al.*<sup>4</sup> suggest is the stable phase of the system.

To establish the compositions of the two f.c.c. phases, two alloys were cast having compositions represented by the formulae  $\text{MgLiZn}$  and  $\text{MgLi}_2\text{Zn}$ , respectively. The former was single-phase, the X-ray pattern showing a f.c.c. structure with  $a = 7.4400$  Å. This meant that the second f.c.c. phase found in the annealed 7½% zinc alloy was  $\text{MgLiZn}$ . The diffraction pattern for the second alloy cast was more complex. The principal phase was f.c.c. of the  $B32$  ( $\text{NaTi}$ )-type, with  $a = 6.266$  Å. A small amount of the  $\beta$  solid solution was also present. The remaining faint reflections corresponded with those normally associated with  $\theta$  and  $\text{MgLi}_2\text{Zn}$ , respectively. A survey of the relevant binary equilibrium diagrams shows that only one phase ( $\text{LiZn}$ ) has a  $B32$ -type structure, the lattice parameter of which is quoted as 6.208 Å. It is thus possible that the principal f.c.c. phase found in the alloy cast to the composition  $\text{MgLi}_2\text{Zn}$  is derived from  $\text{LiZn}$ . It is of interest to note that the suggested formula for the  $\theta$  phase ( $\text{MgLi}_2\text{Zn}$ ) may possibly be derived from  $\text{LiZn}$  simply by replacing half the zinc atoms by magnesium in a manner similar to that suggested by Busk<sup>4</sup> for the formation of  $\text{MgLi}_2\text{Al}$  from



AlLi. As it was not possible to cast an alloy consisting only of the compound  $\text{MgLi}_2\text{Zn}$ , it would appear that a ternary phase of this composition does not exist under normal conditions. This may mean that: (a)  $\theta$  is a transitional structure, and/or (b) that this phase does not correspond to the suggested composition. In recent work on phase relationships in magnesium-lithium-zinc alloys, Weinberg, Levinson, and Rostoker<sup>5</sup> state that the  $\theta$  phase is  $\text{MgLi}_2\text{Zn}$  and that at no temperature did they observe the (hypothetical) compound  $\text{MgLi}_2\text{Zn}$  metallographically, though evidence of its presence was found in many specimens by X-ray diffraction methods. In all cases it occurred in addition to the other phases found metallographically. Weinberg *et al.* concluded that the hypothetical  $\text{MgLi}_2\text{Zn}$  may be a metastable strain-induced phase developed by the powdering operation in preparing the X-ray specimens. In the present work small specimens subsequently heat-treated and then chemically etched to slivers were used, thus avoiding any strain-induced constituents.

To prove that the  $\theta$  phase is transitional and exists only in metastable alloys, experiments were made to determine the equilibrium conditions existing in the ternary  $7\frac{1}{2}\%$  zinc alloy at various temperatures over the range  $100^\circ$ – $450^\circ\text{C}$ . Specimens were quenched into cold water after being maintained for suitable times at the required temperature. X-ray examination showed that: (a) from  $450^\circ\text{C}$ . to  $300^\circ\text{C}$ . the alloy was composed of a single-phase b.c.c.  $\beta$  solid solution, (b) at  $250^\circ\text{C}$ . it was near the phase boundary ( $\beta$  solid solution and a little  $\text{MgLi}_2\text{Zn}$ ), and (c) from  $200^\circ$  to  $100^\circ\text{C}$ . it consisted of two phases ( $\beta$  solid solution and  $\text{MgLi}_2\text{Zn}$ ). Neither  $\alpha$  nor  $\theta$  was observed after treatment at any temperature. It should be mentioned that at the lower temperatures ( $100^\circ$  and  $150^\circ\text{C}$ .) specimens were first annealed at  $300^\circ\text{C}$ . in the single-phase region and then cooled at an average rate of  $1\frac{1}{2}^\circ\text{C}/\text{hr}$ . to the required temperature and maintained there for 24 hr. before being quenched into water. Attempts to cool at faster rates produced alloys which were not in equilibrium and contained both  $\alpha$  and  $\theta$ . Annealing an alloy containing  $\theta$  below  $150^\circ\text{C}$ . for 500 hr. did not produce equilibrium. Rowland, Armantrout, and Walsh<sup>6</sup> have found that the  $\theta$  phase  $\text{MgLi}_2\text{Al}$  does not exist in the magnesium-lithium-aluminum system in the range  $100^\circ$ – $400^\circ\text{C}$ . The present experiments indicate that in the  $7\frac{1}{2}\%$  zinc ternary alloy the precipitating phase is transitional and changes rapidly to the stable phase  $\text{MgLi}_2\text{Zn}$  after quenching in water and ageing above about  $150^\circ\text{C}$ . Below this temperature, however, precipitated  $\theta$  appears to possess considerable stability, e.g. it persisted after ageing for 168 hr. at  $125^\circ\text{C}$ . Its composition is uncertain, although the formation of the  $\alpha$  phase indicates that  $\theta$  is probably a lithium-rich compound. The decrease in lattice parameter of  $\theta$  during ageing suggests a change in composition; this may be caused by a rejection of lithium atoms, as suggested by Jackson *et al.*<sup>3</sup> and by Freeth and Raynor.<sup>7</sup>

The addition of 1 at.-% silver to the ternary zinc alloy produced little change in the diffraction patterns when the alloy was aged at  $50^\circ$  or  $75^\circ\text{C}$ . However, ageing at  $16^\circ\text{C}$ . (at which temperature the alloy containing silver is stable), gave only a few broad reflections on the X-ray patterns from the  $\theta$  phase, even after ageing for 3 months. The lattice parameter of the  $\beta$  solid

solution was decreased by the addition of silver; immediately after quenching from  $450^\circ\text{C}$ . the value was  $3.4940\text{ \AA}$ . compared with  $3.5017\text{ \AA}$ . for the ternary alloy. The chief difference in structure caused by the addition of silver is that, under tests identical with those carried out with the basic ternary alloy, no evidence could be found for the existence of an equilibrium phase corresponding to  $\text{MgLi}_2\text{Zn}$ . From  $450^\circ$  to  $250^\circ\text{C}$ . the quaternary alloy consisted of a single phase ( $\beta$  solid solution); from  $250^\circ$  to  $100^\circ\text{C}$ . the quaternary alloy consisted of two phases ( $\beta + \theta$ ). The lattice parameter of  $\theta$  in the alloy containing silver is  $6.674\text{ \AA}$ . No hexagonal  $\alpha$  phase was observed in the equilibrium structures. It thus appears that silver, because of its lower valency, stabilizes the  $\theta$  phase. However, in the aged condition  $\theta$  behaved in a similar way to the  $\theta$  phase in the basic ternary zinc alloy, in that a decrease in lattice parameter occurred and some  $\alpha$  was associated with the  $\theta$ . The decrease in lattice parameter of the  $\theta$  phase in the quaternary alloy containing silver was, however, not so great. Further, the quantity of  $\alpha$  was only just sufficient to give rise to a diffraction pattern. Some of the X-ray-diffraction patterns are shown in Figs. 16 and 17 (Plates XLV and XLVI).

When examined under the microscope in the as-quenched condition, the ternary alloy with  $7\frac{1}{2}\%$  zinc showed equiaxial grains of the  $\beta$  solid solution with fine grain boundaries. Little change in microstructure occurred on ageing until just before maximum hardness was reached, when localized precipitation appeared at the grain boundaries. In the ternary alloy this consisted of isolated particles of the  $\theta$  phase  $\text{MgLi}_2\text{Zn}$ , but in the quaternary alloys containing silver or copper  $\theta$  formed a continuous network around the grain boundaries (Figs. 6–8, Plate XLIV), and was responsible for the brittleness occurring in these alloys. At the same time as the grain-boundary precipitation, "roughening" of the  $\beta$  grains took place, assumed to represent the first stages of general precipitation. As ageing proceeded to the point of maximum hardness, the roughening changed into a fine granular precipitation (Fig. 9, Plate XLIV). Further ageing past the point of maximum hardness produced a change in the etching characteristics of the alloy. In the regions of general precipitation, particularly at the junctions of grain boundaries, "darkening" occurred, and these areas spread to occupy the whole grains as ageing proceeded (Figs. 10 and 11, Plate XLIV). This occurred while the lattice parameter of the  $\theta$  phase was decreasing. Prolonged ageing produced a growth of the grain-boundary particles and also of those within the grains. In a few localized areas, instead of granular precipitation of a general nature, precipitation followed definite directions within the grains (Figs. 12 and 13, Plate XLIV).

The ageing sequence described occurred with the basic ternary zinc alloy and the quaternary alloy containing copper, at all ageing temperatures studied. The mechanism was the same for the quaternary alloy containing silver at  $50^\circ$  and at  $75^\circ\text{C}$ ., but at  $16^\circ\text{C}$ ., when this alloy is stable, little change in microstructure, apart from roughening and some grain-boundary precipitation, was observed. Silver had a grain-coarsening effect on the basic ternary zinc alloy, illustrated by comparing Figs. 14 and 15 (Plate XLIV), which show  $\theta$  in the quaternary alloy (Fig. 15) and the equilibrium phase



MgLiZn in the basic ternary alloy (Fig. 14). Both structures are from specimens water-quenched from 200° C.

## VI.—GENERAL DISCUSSION

The results of the experiments show that the instability of the mechanical properties of the high-strength magnesium-lithium-base alloys may be connected with electron concentration. Lowering the electron concentration by suitable additions decreased the instability, silver (univalent) being the most effective addition. The properties of the basic ternary zinc alloy and ternary cadmium alloys were stabilized at 16° C. by the addition of 1 at.-% silver. Copper is also effective as a stabilizing agent, particularly when added to the alloys containing cadmium. Both silver and copper increased the strength of the ternary alloys, and after suitable treatments mechanical properties were obtained superior to those of most other magnesium alloys in commercial use. Even though the alloys containing silver or copper were not stable above 16° C., the mechanical properties after ageing for 200 hr. at 75° C. are nevertheless encouraging. The optimum mechanical properties obtained with the quaternary alloys are given in Table V for those alloys found to be stable at 16° C.

The hardening in the alloy containing 7½% zinc is caused by the precipitation of a transitional phase  $\theta$  which has tentatively been given the formula  $\text{MgLi}_2\text{Zn}^2$ . The equilibrium phase of the alloy below 250° C. was found in these experiments to be the ternary compound MgLiZn. It has been suggested that the composition of the  $\theta$  phase<sup>7</sup> moves towards equilibrium during ageing by the rejection of lithium atoms, but a simple

TABLE V.—*The Optimum Mechanical Properties of the Quaternary Alloys Stable at 16° C. (Mg:Li = 88:12).*

Composition	Condition	L.P., tons/ in. <sup>2</sup>	0.1% P.S., tons/ in. <sup>2</sup>	U.T.S., tons/ in. <sup>2</sup>	Elong. on 2 in., %
18% Cd + 1 at.-% Ag	Hot rolled	7½	12½	21½	10
	Hot rolled, aged at 75° C. for 200 hr.	4½	7½	17	30
	W.Q. from 450° C., aged at 75° C. to max. hardness	8	11½	22½	5
18% Cd + 1 at.-% Cu	Hot rolled	6½	10½	18½	20
	Hot rolled, aged at 75° C. for 200 hr.	3½	6½	15½	25
	W.Q. from 450° C., rolled to max. hardness	14½	18½	24	10
7½% Zn + 1 at.-% Ag	Hot rolled	6	10	16½	30
	Hot rolled, aged at 75° C. for 200 hr.	4½	7½	14½	40
	W.Q. from 450° C., aged at 75° C. for 200 hr.	7½	10½	15½	10
	Cold rolled	9	12	17½	35

transformation of the  $\theta$  phase into MgLiZn brought about by the rejection of sufficient lithium is difficult to visualize. Such a change would involve an increase in the lattice parameter of  $\theta$  and not a decrease, as has been found to occur. Furthermore, it is doubtful whether MgLiZn has the same crystal structure. From the results obtained, it is possible to suggest a mechanism for the transformation. The initial  $\theta$  precipitate may absorb sufficient lithium from the  $\beta$  matrix to approximate to the formula  $\text{MgLi}_2\text{Zn}$ . This view is strengthened by the formation of the hexagonal  $\alpha$  phase

at this stage (observed in the X-ray diffraction patterns). During ageing  $\theta$  loses this lithium, and the lattice parameter decreases to a minimum of 6.6660 Å., at which stage it is suggested that the composition of the precipitated phase ( $B_{32}$  structure) approximates to MgLiZn. When the lattice parameter has decreased to 6.6660 Å., the phase exists almost indefinitely at ordinary temperatures, and it is only when the temperature is raised above about 150° C. that the metastable phase undergoes a change into the equilibrium phase MgLiZn (lattice parameter = 7.440 Å.) of undetermined crystal structure. Lowering the electron concentration by the addition of silver enables the  $\theta$  phase of the quaternary alloy to become the equilibrium phase. Even so, the  $\theta$  phase at precipitation appeared capable of dissolving excess lithium, later rejected during ageing at temperatures higher than normal. The cause of hardening appears to be nothing more than a pre-precipitation phenomenon, and it would seem that the formation of visible precipitate would cause overageing and softening. In view of this, the change in lattice parameter of the  $\theta$  phase is not necessarily the main cause of softening.

## VII.—CONCLUSIONS

This investigation deals with the stability of mechanical properties of the high-strength  $\beta$ -phase magnesium-lithium alloys at temperatures up to 75° C. Stability was obtained at 16° C. and a diminished instability at 75° C. It would appear that instability is related in some way to the valency of the added fourth metal (or more correctly the electron:atom ratio of the alloy), an effect more noticeable if the "effective" valency rather than the chemical valency is considered. Experiments to illustrate this connection show that silver, added to decrease the electron concentration, produced the greatest effect by stabilizing the mechanical properties of ternary alloys containing 7½% zinc and 9% and 18% cadmium, respectively, whilst antimony, added because it was thought to raise the electron concentration, increased instability.

Although improvements in stability were effected, it was only at 16° C. that complete stability was achieved. None of the alloys maintained its hardness for more than 24 hr. on ageing at either 50° or 75° C. Alloys containing cadmium were less unstable than those containing zinc. If lowering the electron concentration of the alloys is the only means by which instability can be decreased, it is difficult to see how stability at 75° C. can be obtained, particularly as 14.3 wt.-% (3 at.-%) of silver, when added to the basic ternary magnesium-lithium-zinc alloy, provided stability of properties only for 24 hr. at 75° C. This, however, is a much longer period than with the basic ternary alloy.

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# NOTE ON THE EFFECT OF ADDITIONS OF MANGANESE AND CHROMIUM ON THE MICROSTRUCTURE OF D.T.D. 687A-TYPE ALLOYS \*

By (Miss) M. K. B. DAY,† M.A., A.Inst.P., A.I.M., MEMBER

## SYNOPSIS

Additions of manganese and/or chromium have to be made to D.T.D. 687A-type alloys in order to obtain the required mechanical properties, but experience has shown that in some alloys such additions can cause serious trouble owing to the formation of brittle segregates. The microstructures of a number of slowly cooled melts of basic composition Zn 5.75, Mg 2.5, Cu 1.25, Fe 0.2, Si 0.2%, containing small quantities of manganese and chromium, have therefore been examined, and the boundary of the primary aluminium phase field determined. The limits of this field conform to the rough approximation that the sum of the manganese content plus three times the chromium content must not exceed 1%. In melts of higher iron content, the effective manganese content should be regarded as the sum of the actual manganese content together with the iron content in excess of 0.2%.

## I.—INTRODUCTION

In order to attain the required mechanical properties in D.T.D. 687A-type alloys it is necessary to add small quantities of manganese or chromium, but such additions may lead to serious trouble in some cases owing to the formation of brittle segregates. For this reason, before the possibility of adding these elements simultaneously to D.T.D. 687A alloy was explored on a production scale, a small investigation was carried out to determine their effect on the microstructure of the alloy. The work was limited to a determination of the limits of the primary aluminium phase field when additions of manganese and chromium were made to melts having a basic D.T.D. 687A type of composition, the melts subsequently being allowed to cool slowly.

## II.—RANGE OF MELTS EXAMINED

The basic composition aimed at was Zn 5.75, Mg 2.5, Cu 1.25, Fe 0.2, Si 0.2%, and additions were made within the ranges 0.1–2% manganese and 0–0.5% chromium. Melts of 200 g. were allowed to cool at the rate of 4°–7° C./min. Under production conditions of semi-continuous casting, the rate of chilling would be faster, in which case a slightly greater degree of supersaturation might be expected, but the slow rate was adopted because it allows a margin of safety in applying the results to commercial practice.

Preliminary work had shown that a brittle primary intermetallic constituent made its appearance when 0.5% iron was added to a superpurity-base D.T.D. 687A type of alloy containing 0.6% manganese. In view of this, a few melts were examined in which the iron contents had been increased from 0.20%, the normal level in commercial alloys, to 0.55%, the highest level ever likely to be encountered in commercial practice.

## III.—DISCUSSION AND RESULTS OBTAINED

The experimental results and the boundary of the primary aluminium phase field are shown in Fig. 1. No attempt has been made to plot the boundaries between the primary intermetallic phase fields, or to identify them all individually, although this is discussed further below.

### (a) *Effect of Manganese*

Primary crystals of  $\text{MnAl}_6$  containing some iron in solid solution<sup>1</sup> were identified in melts containing manganese in excess of about 0.95%. There was no evidence that the crystals had reacted peritectically to form ternary or more complex compounds; this was in agreement with published information on the systems Al–Cu–Mn<sup>2</sup> and Al–Mg–Mn–Zn.<sup>3</sup>

### (b) *Effect of Chromium*

When additions of 0.38% chromium or more were made, coarse duplex crystals appeared, which were in the form of irregular rounded masses. When secondary, the chromium-bearing phase appeared as short needles.

Work on the system Al–Cr–Mg,<sup>4</sup> and published data on the systems Al–Cr–Mg–Zn,<sup>5</sup> Al–Cr–Zn,<sup>6</sup> and Al–Cr–Fe,<sup>7</sup> indicate that the duplex crystals consist of cores of  $\text{CrAl}_7$ , which can take zinc and iron into solid solution, surrounded by a ternary compound of variable composition  $\alpha(\text{CrMg})$ . No ternary compounds appear to be formed in the system Al–Cr–Cu.<sup>8</sup>

### (c) *Effect of Manganese and Chromium Together*

Data on the system Al–Cr–Mn<sup>9</sup> show that chromium is practically insoluble in  $\text{MnAl}_6$ , but that  $\text{CrAl}_7$  and  $\text{Cr}_2\text{Al}_{11}$  can dissolve appreciable quantities of manganese. Complex D.T.D. 687A-type alloys of high manganese content contained primary constituents of the  $\text{MnAl}_6$

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form, but typical rounded masses of the chromium-bearing type were found in melts of lower manganese content. The ternary Al-Cr-Mn compound designated

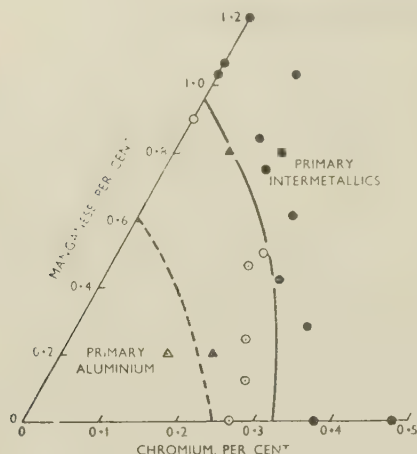
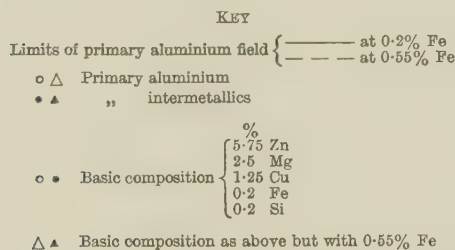


FIG. 1.—Limits of Primary Aluminium Field.



$G^{9,10}$  would not be expected to occur in these slowly cooled alloys.

#### (d) *Effect of Increasing the Iron Content*

X-ray powder-diffraction patterns of crystals extracted electrolytically from higher iron-bearing, chromium-free alloys showed that these crystals were similar in form to  $MnAl_6$ , and chemical analysis indicated that their composition approximated to the formula  $(FeMn)Al_6$ . Evidence was obtained that iron could replace manganese beyond the limiting composition of  $(\frac{1}{2}Fe\frac{1}{2}Mn)Al_6$  suggested by Raynor,<sup>1</sup> and in one sample the ratio iron : manganese had a value of 1.8. This led to the

conclusion that a higher iron content had the result of increasing the effective manganese content; so in the chromium-free alloys, since the limit of the primary aluminium field was 0.96% manganese at an iron content of 0.2%, the corresponding limit at 0.55% iron was taken to be 0.61% manganese.

Taking into account the fact that iron has only a limited solubility in  $CrAl_7$ ,<sup>1</sup> the same assumption was also applied to the alloys containing some chromium, and the boundary of the primary aluminium field for an iron content of 0.55% was interpolated from that determined for 0.2% iron. The interpolation would appear to be justified, at least as far as an iron : manganese ratio of 1.8, that is, down to a manganese content of 0.3%. Then, since a continuation of the interpolated curve passed between two of the experimental points obtained for alloys of higher iron content, the curve was continued until it intercepted the chromium axis and is shown dotted in Fig. 1.

#### IV.—CONCLUSIONS

In the slowly cooled D.T.D. 687A-type alloys examined, the limits of the primary aluminium field conformed to the rough approximation that, if the presence of brittle segregates is to be avoided, the sum of the manganese content plus three times the chromium content must not exceed 1%. In melts of higher iron content, the effective manganese content should be regarded as the sum of the actual manganese content together with the iron content in excess of 0.2%.

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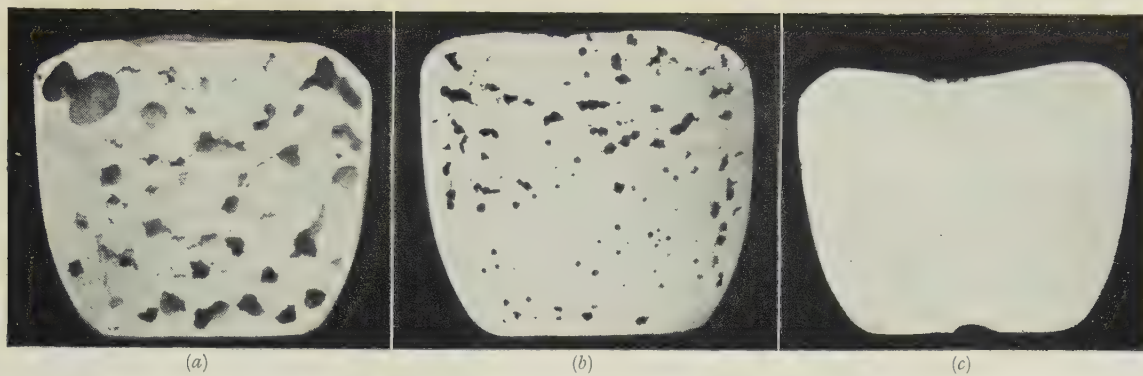


FIG. 1 (a)-(c).—Sections Cut Through Gas-Test Specimens of LM14 (Y Alloy).

- (a) Sample showing gross gas porosity.  
 (b) Sample from same melt as (a), taken during degassing operation.  
 (c) Sample from same melt, 5 min. after completion of degassing operation.

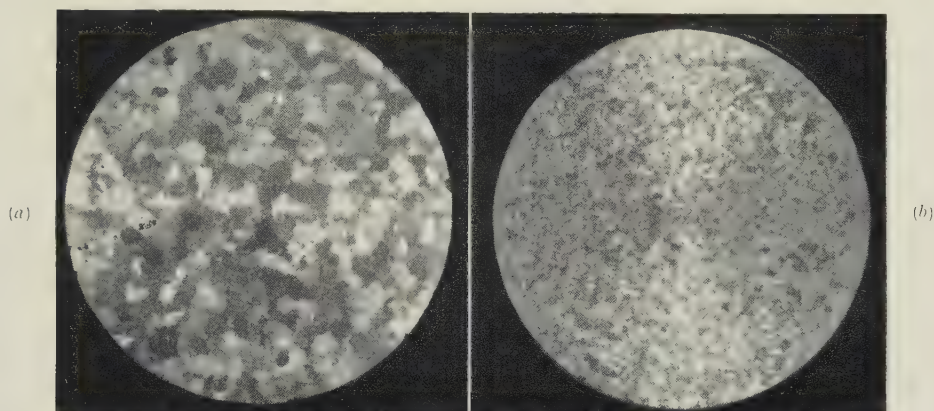


FIG. 2.—Cross-Section of 1-in. D.T.D.-Type Test-Bars in LM4.  $\times 3$ . (a) Showing coarse grain-size before grain refining. (b) Similar specimen from same melt after grain refining.

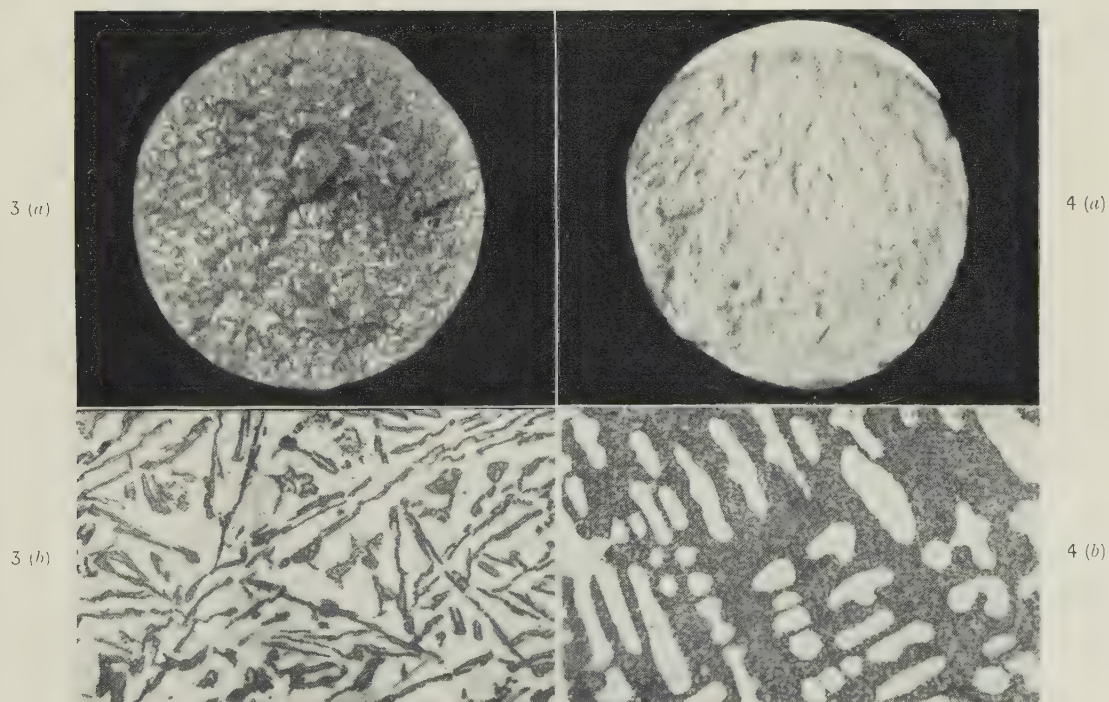


FIG. 3 (a).—Fracture of LM6 Sand-Cast Test-Bar in Unmodified Metal.

FIG. 3 (b).—Photomicrograph of Sand-Cast Specimen from LM6 Melt, Showing Coarse Structure Resulting from the Unmodified Condition.  $\times 200$ .

FIG. 4 (a).—Fracture of LM6 Sand-Cast Test-Bar from Same Melt as Fig. 3 (a), After Modification by "Salts" Method.

FIG. 4 (b).—Photomicrograph of Sand-Cast Specimen from LM6 Melt, Showing Effect due to Modification.  $\times 200$ .

RADIOGRAPHS OF ALUMINIUM ALLOY SPECIMENS

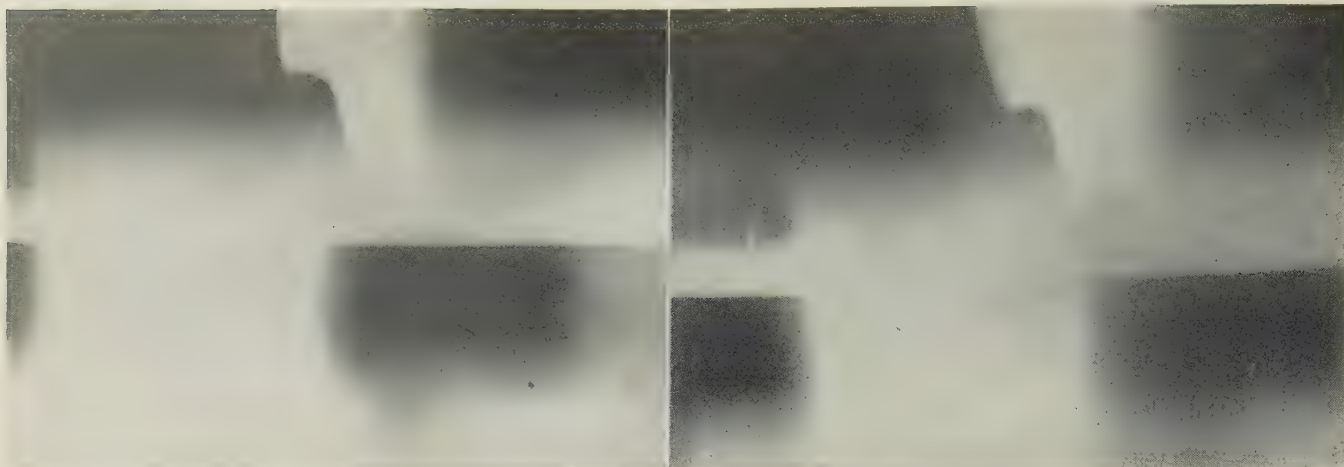


FIG. 5 (a).—Showing Severe Internal Shrinkage Fissure (Draw).

FIG. 5 (b).—Similar Casting Illustrating Beneficial Effect of Local Chill.

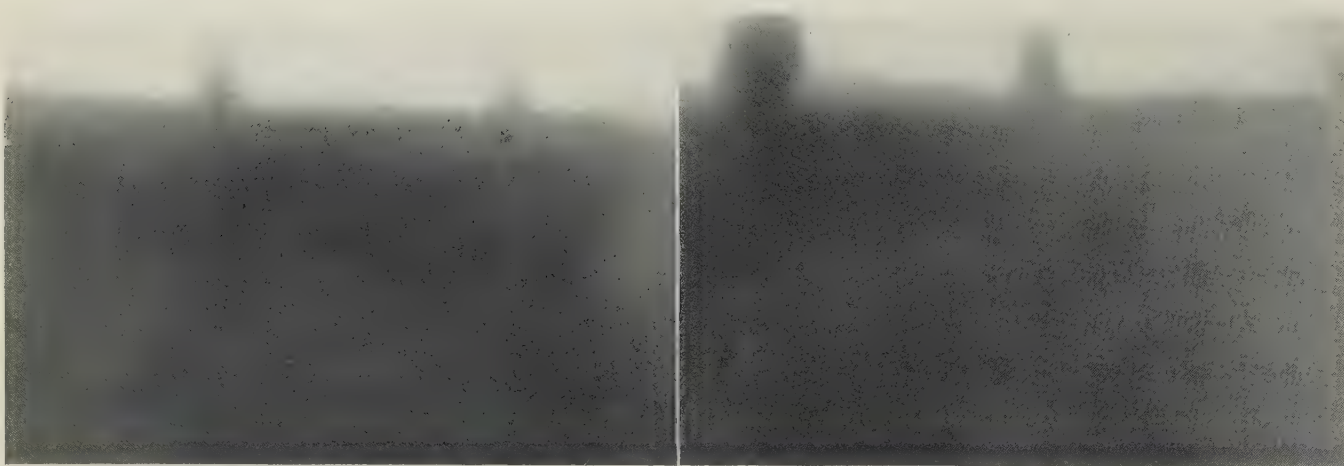


FIG. 6 (a).—Sub-Surface Porosity, due to Mould Reaction, in LM5.

FIG. 6 (b).—Similar Area, Corrected by Use of Inhibitors in the Sand Mix.

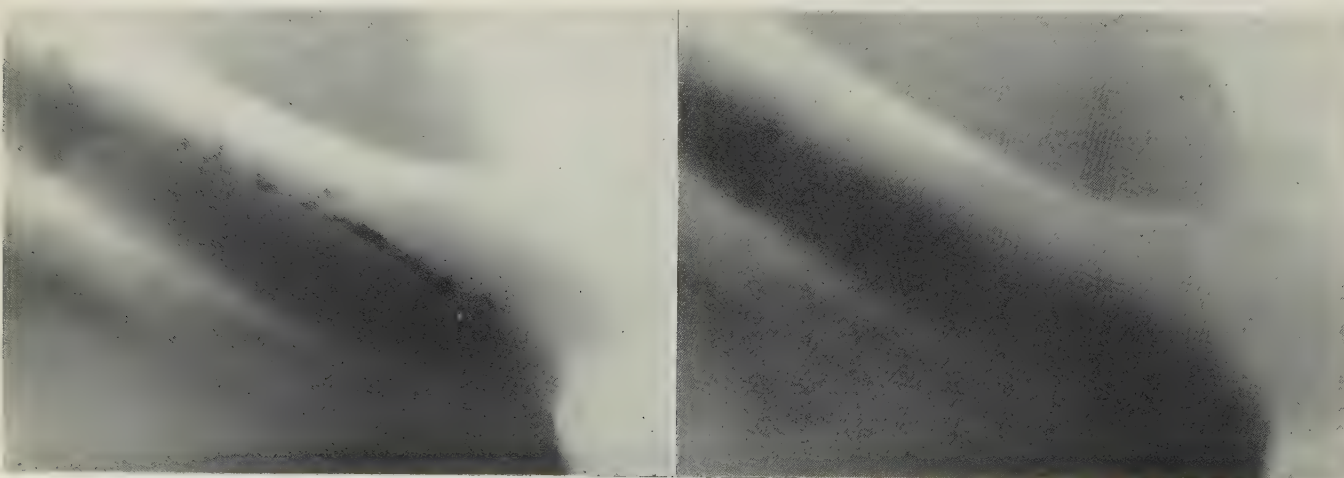
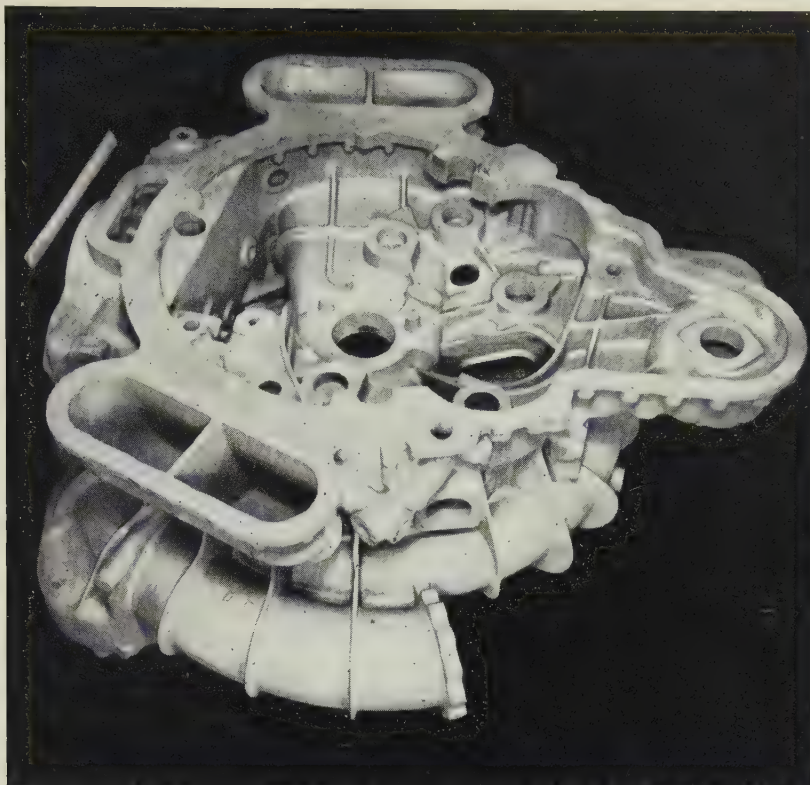


FIG. 7 (a).—Section of a Large Lightly Stressed Casting in LM14, Showing Unsoundness on Rib due to Blow Holes. The fault was not observable by normal visual inspection.

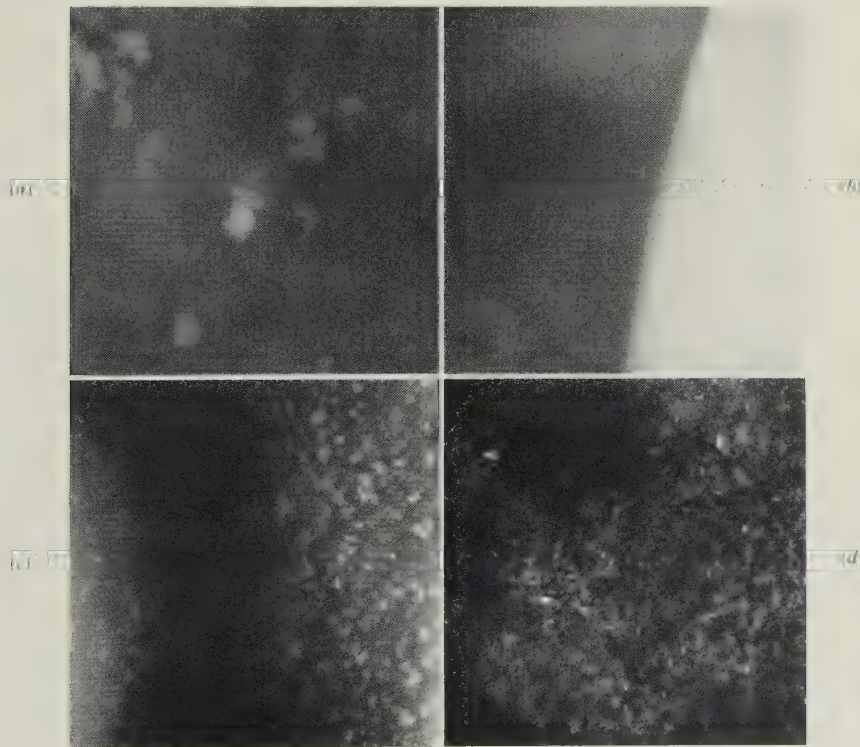
FIG. 7 (b).—Area as Above, Showing Repair Effected by Welding.





[Courtesy Sterling Metals, Ltd.]

FIG. 1.—Aircraft Supercharger Casting in Meltron ZRE1 Weighing Approx. 350 lb. and Incorporating over 50 Cores. Note 12-in. rule in top left-hand corner.



FIGS. 2 (a)–(d).—Characteristic Radiographic Appearance of Certain Defects, &c., When Occurring in Magnesium-Zirconium Alloys ( $\frac{1}{8}$ -in.-thick sections). (a) Oxide skins; (b) Variation in radiographic density in substantially uniform section; (c) Sand inclusions; (d) Zr-rich particles. (Extreme examples produced by poor practice.)



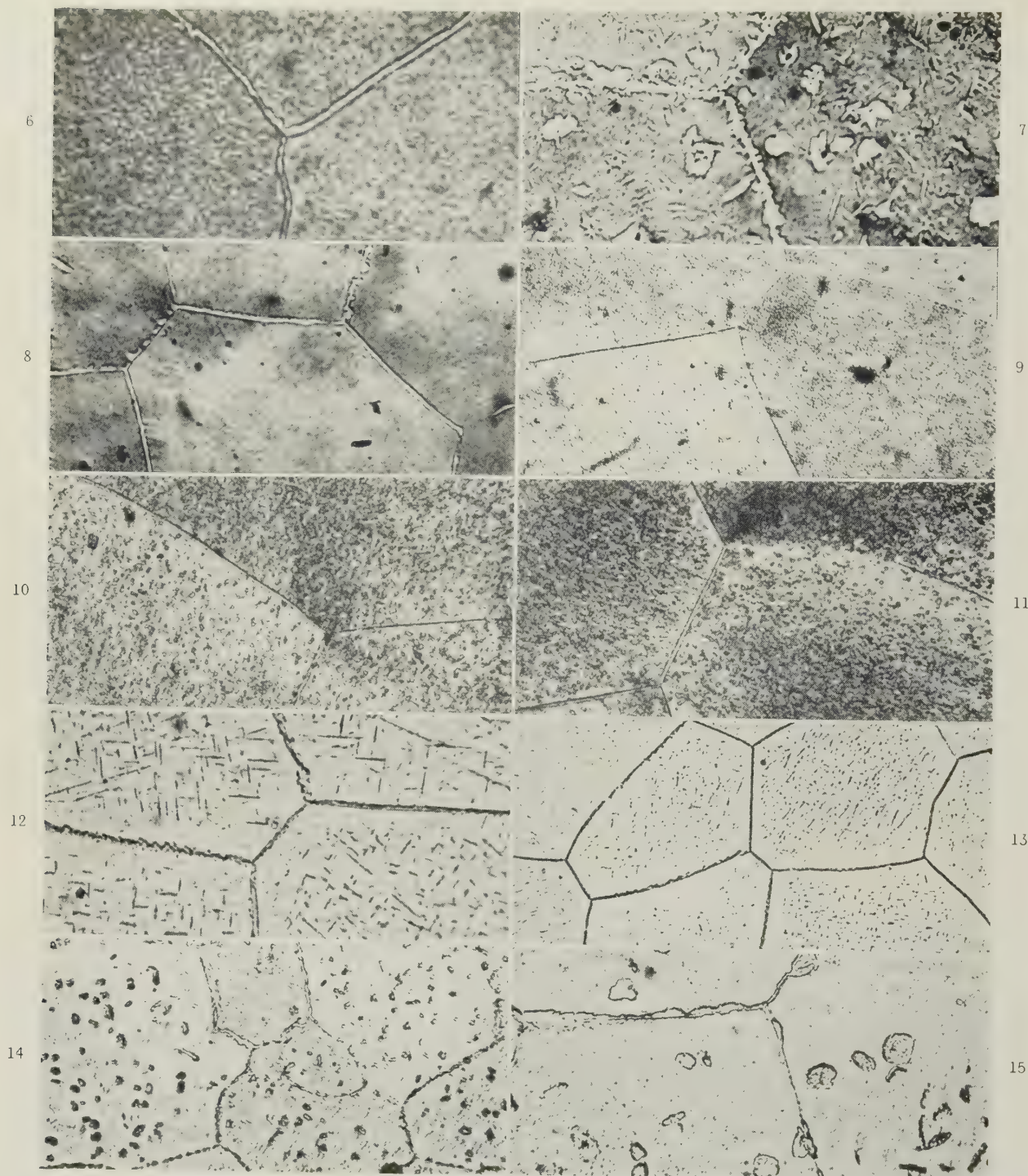
PHOTOMICROGRAPHS OF ALLOY OF BASIC TERNARY COMPOSITION  $Mg:Li = 88:12$ ,  $Zn\ 7\frac{1}{2}\%$ 

FIG. 6.—Basic Alloy + 2 at.-% Ag. W.Q. from 450° C., aged at 75° C. to maximum hardness. Electrolytically polished and etched.  $\times 1600$ .

FIG. 7.—Basic Alloy + 2 at.-% Ag. W.Q. from 450° C., aged 200 hr. at 75° C. Electrolytically polished and etched.  $\times 600$ .

FIG. 8.—Basic Alloy + 1 at.-% Ag. W.Q. from 450° C., aged 200 hr. at 75° C. Electrolytically polished and etched.  $\times 600$ .

FIG. 9.—Basic Alloy. W.Q. from 450° C., aged to maximum hardness at 75° C. Electrolytically polished and etched in 3% nital for 15 sec.  $\times 600$ .

FIG. 10.—Basic Alloy. W.Q. from 450° C., aged 56 min. Electrolytically polished and etched in 3% nital for 15 sec.  $\times 600$ .

FIG. 11.—Basic Alloy. W.Q. from 450° C., aged at 75° C. for 18 hr. Electrolytically polished and etched in 3% nital for 15 sec.  $\times 600$ .

FIG. 12.—Basic Alloy. W.Q. from 450° C., aged at 75° C. for 4 days. Electrolytically polished and etched in 3% nital for 15 sec.  $\times 600$ .

FIG. 13.—As for Fig. 12.  $\times 250$ .

FIG. 14.—Basic Alloy. W.Q. from 200° C. Electrolytically polished and etched.  $\times 600$ .

FIG. 15.—Basic Alloy + 1 at.-% Ag. W.Q. from 200° C. Electrolytically polished and etched.  $\times 600$ .



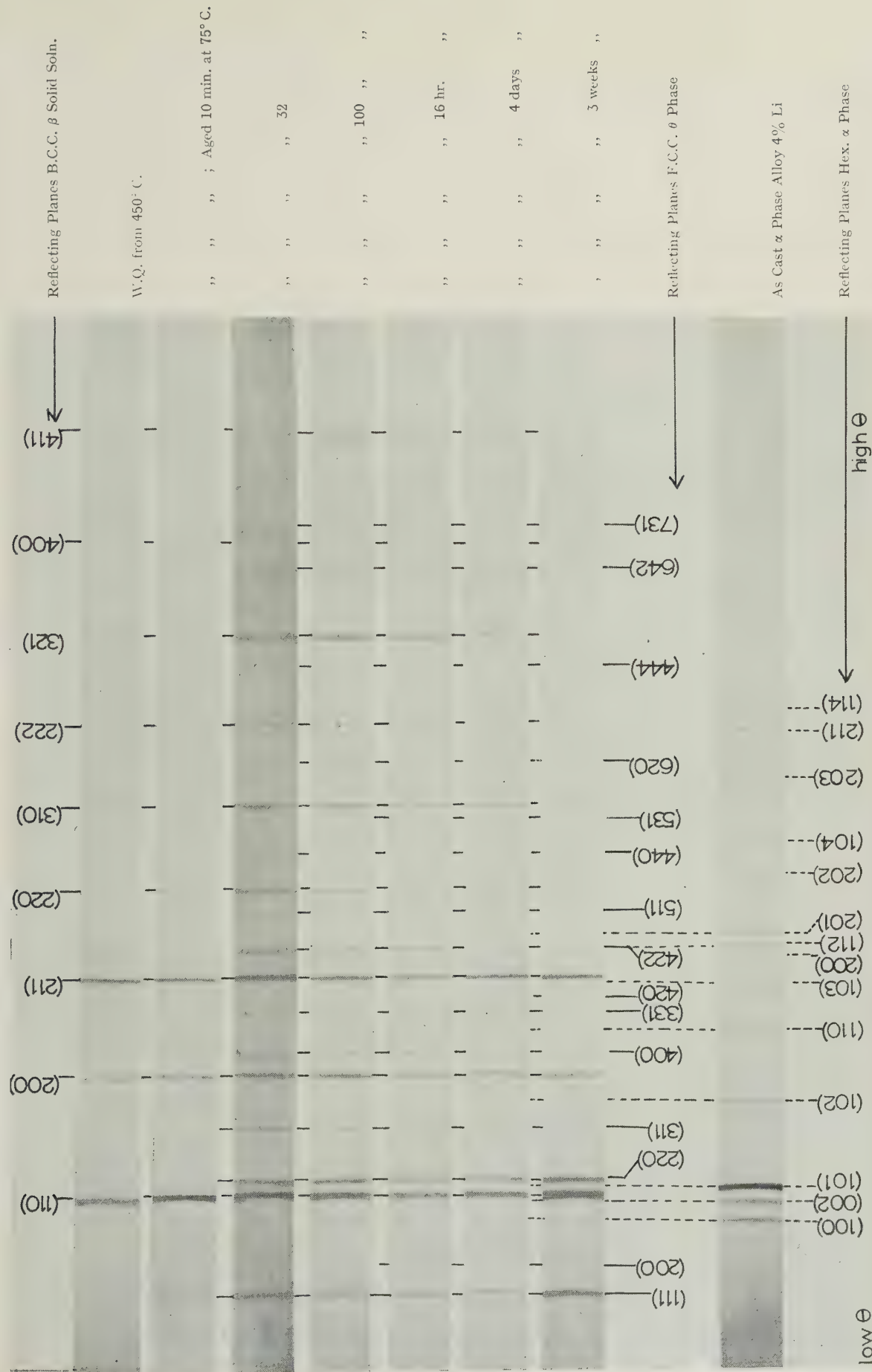


FIG. 16.—Diffraction Patterns for Alloy of Basic Ternary Composition Mg:Li = 88:12, Zn 7½%. Water-Quenched from 450° C. Aged at 75° C. 19-cm. camera,  $\text{CuK}_\alpha$  radiation.

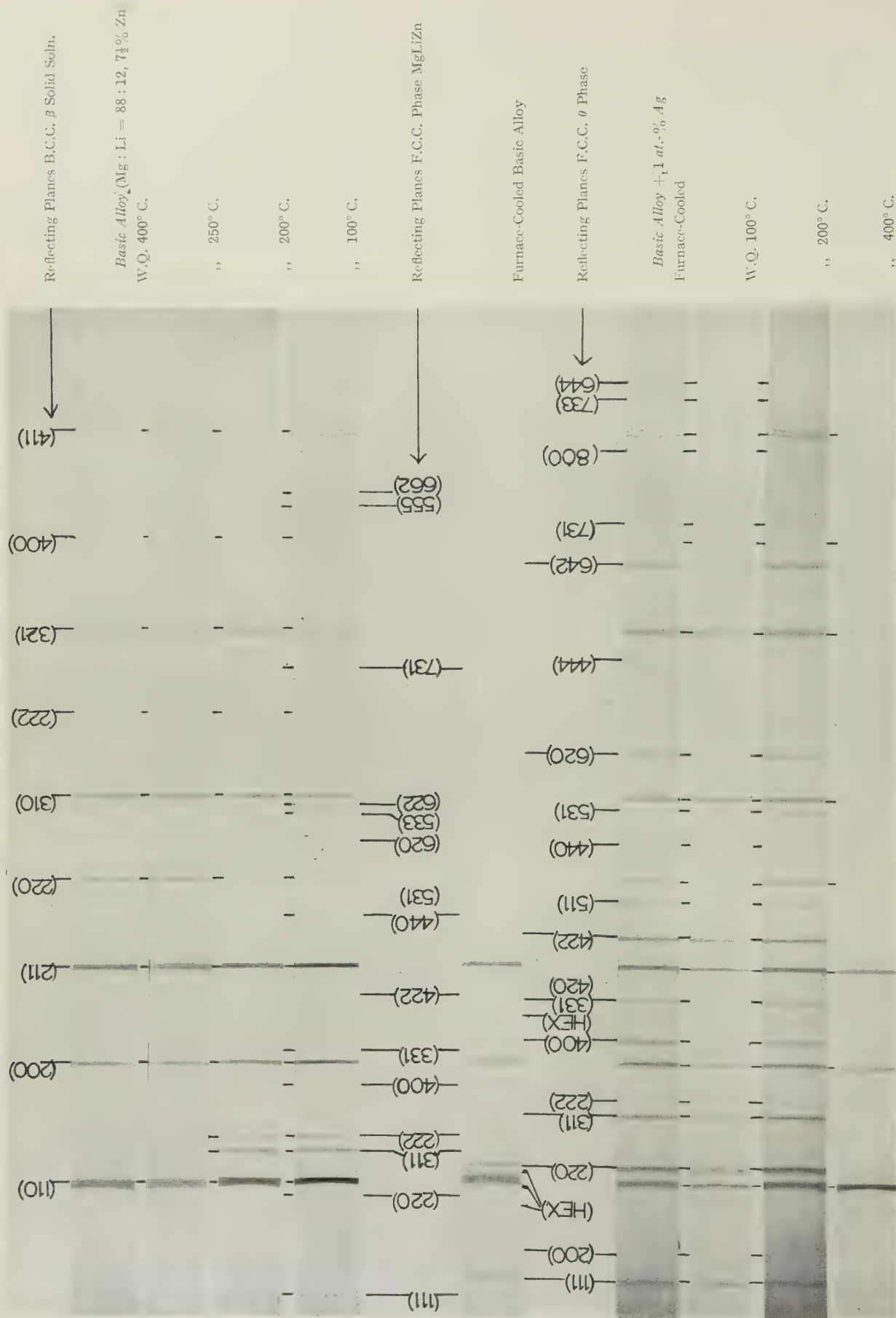


FIG. 17.—Diffraction Patterns for Alloy of Basic Ternary Composition Mg : Li 88 : 12, Zn 7½%, and Same Alloy + 1 at.-% Ag, Showing Equilibrium Phases. 19-cm. camera,  $\text{CuK}\alpha$  radiation.



# THE METALLURGICAL PRINCIPLES OF THE CONTROL OF QUALITY OF NON-FERROUS CASTINGS \*

1749

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(Communication from The British Non-Ferrous Metals Research Association)

## SYNOPSIS

The paper reviews the reasons for the occurrence of defects in castings and the scientific basis of methods for the avoidance of these defects. Subjects discussed include:

- (a) The flow of liquid metals through the gating system and into the mould cavity.
- (b) The rate at which castings freeze, the mechanisms of freezing in metals and alloys, and the bearing of these factors on the incidence of shrinkage porosity and on methods of feeding. Other defects arising during solidification, such as hot tears and segregation, are also considered.
- (c) Melt quality, including the control of gas content, grain refinement, elimination of non-metallic inclusions, and test-bar design.

## I.—INTRODUCTION

KNOWLEDGE of the fundamental metallurgy involved in the production of castings is clearly vital when considering the steps taken to control the quality of sand-castings, for without this fundamental background quality control must necessarily be a haphazard matter of trial and error. There are several prerequisites for the production of serviceable castings. In the first place the metal or alloy must be free from gas and from non-metallic inclusions when it is poured into the mould. Secondly, in its journey through the running system the liquid metal must neither absorb or entrain mould gases nor produce dross by reaction with these gases; in addition, violent impingement of the flowing liquid on the mould or cores must be prevented to avoid the possibility of sand inclusions and damage to the mould. Thirdly, the conditions of freezing within the mould cavity must be such that shrinkage porosity is eliminated or at least reduced to a small quantity of a harmless type; this in general involves disposing the runners, chills, and feeders in such a way that a pattern of solidification suited to the particular alloy and casting is assured. Furthermore, segregation of alloying elements during freezing must be avoided, and so must hot tearing and gas pick-up from the mould (mould reaction). The metal must be poured at a temperature suited to its characteristics, so that it can fill the mould cavity completely and thus preserve dimensional accuracy in the solid casting. A good surface finish is an important factor with many castings; in particular, large patches of dross or sinks on the surface are highly undesirable. If good mechanical properties are to be obtained, not only must the metal be substantially gas-free when poured, but steps must often be taken to ensure that the casting solidifies to yield a suitable grain structure.

The basic metallurgical factors governing all these requirements are discussed below under three main headings: Section II deals with the flow of liquid metals in the gating system and during the filling of the mould cavity. Heat flow in the casting and mould and the mechanism of freezing are discussed in Section III; important practical matters such as feeding practice, segregation, grain refinement, and hot tearing are also considered. Section IV covers a number of factors intimately connected with the mechanical properties of the final casting, including control of the gas content of the liquid metal, control of the grain-size of the casting, and means of avoiding the presence of non-metallic inclusions.

The control of those defects which arise from faulty selection, preparation, and ramming of the sand are outside the scope of the present symposium and are not discussed.

## II.—THE FLOW OF LIQUID METALS

### 1. THE GATING SYSTEM

#### (a) *The Functions of the Gating System and Its Influence on Casting Quality*

An analysis of the defects in rejected castings suggests that greater attention to gating practice is often a most rewarding measure in the control and improvement of casting quality.<sup>1,2</sup> Unfortunately, there is frequent disagreement on the merits of recommended running and gating systems, as these are usually based on individual experience and preference. In recent years, however, a number of systematic studies have been published from which useful conclusions may be drawn on the design of many features of the ideal running system, though it is still far from possible to lay down explicit rules for a

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given casting and alloy. A detailed and critical review of this recent work has been published by one of the present authors,<sup>1</sup> including a theoretical treatment of the flow of liquid metal, which can only be touched on here.

The principal requirement of the running system is that it should not allow turbulence in the stream of metal to exceed the point at which "agitation" occurs, i.e. when the surface is continually broken and the resulting dross is entrained with air in the metal.<sup>3, 4</sup>

Clearly, the permissible degree of agitation varies with the composition of the alloy. Stringent precautions are necessary with all alloys containing aluminium or magnesium, for dross is readily produced and the tenacious oxide films are particularly deleterious; with brasses, gun-metals, and bronzes, on the other hand, much more agitation can be tolerated, particularly in the alloys of high phosphorus content which form only liquid oxidation products. The running system should also be capable of preventing any dross poured with the metal from reaching the mould cavity.

Another important feature of a good running system is that it should limit the velocity of the metal sufficiently to prevent erosion where the stream impinges on the mould surface. This precaution is of greatest importance with the denser metals, such as copper and nickel alloys, as the erosive forces are due to changes in momentum which increases with the density of the metal. The strength of the material in which the runners are moulded should be great enough to withstand any unavoidable impingement.

The position of the gates should allow an adequately smooth flow of metal to be maintained whether the mould cavity is empty or full, and temperature gradients to be set up which minimize shrinkage porosity and distortion.

Finally, the runners should be as short as possible, to avoid the necessity for high pouring temperatures and to reduce the proportion of scrap metal from the runners. If the increase in metal handling and moulding costs is greater than the saving which results from the reduction in the proportion of rejected castings, an elaborate running system is obviously of no advantage, i.e. the economics of the gating system is the deciding factor.

#### (b) The Sprue

The sprue is a common source of dross inclusions and entrained air, largely because the use of too large a cross-section or too slow a pouring rate allows metal to fall freely at a high velocity and splash at the bottom of the sprue. Even if the pouring rate is high enough to enable the entrance to a parallel sprue to be filled, the stream of metal contracts and separates from the mould wall as it gains speed in falling and splashing still occurs; the effects are made worse by the aspiration of air through the mould wall,<sup>5-7</sup> which leads to continual entrainment.

Choking the base, if severe enough to keep the sprue full, avoids the worst defects arising from faulty design, but the sharp reduction in cross-section itself causes excessive turbulence and local erosion due to high metal velocity. Indeed, experimental observations suggest that drossing and other defects at the bottom of the sprue are best avoided by greatly enlarging the cross-section of the base (as discussed below) to reduce the velocity of the metal.<sup>5-9</sup>

The ideal sprue system would probably contain the following features:

(i) *A Pouring Basin.* This should be just large enough to be filled easily without overflowing and deep enough to prevent vortices forming at the exit.<sup>6, 10</sup> The minimum depth to eliminate vortices (usually about 3 in.) should be filled as quickly as possible and the entrance to the sprue should be generously radiused (about 1-1½ in.) to reduce turbulence and, particularly, to avoid the formation of air pockets just below the exit.<sup>5, 11</sup> Pouring directly into the sprue obviously defeats many of the objects of using a pouring basin, one of which is to allow dross carried over from the crucible to separate from the metal stream.

(ii) *A Tapered Sprue.*<sup>5, 6, 10, 11</sup> The taper should be slightly greater than the reduction in cross-section of a metal stream falling freely under gravity, and can be calculated approximately (assuming a straight taper instead of the theoretically curved profile) from the acceleration due to gravity:

$$\frac{\text{Entrance area}}{\text{Exit area}} > \sqrt{\frac{\text{Length of sprue} + \text{depth of pouring basin}}{\text{Depth of pouring basin}}} \quad (1)$$

Some typical sprue entrance and exit diameters are listed in Table I. Too large a taper, leading to excessive choking, is best avoided. The taper, by preventing separation of the metal stream from the mould wall, avoids aspiration and also limits the velocity of the stream by maintaining the frictional resistance to flow at the mould wall. The metal velocity can be reduced still further by increasing the surface area and thus the frictional resistance of the sprue; tapered slot sprues, common in magnesium founding, are probably the most suitable for this purpose,<sup>5</sup> but they present difficulties in moulding, and sprues of circular cross-section are normally adequate.

(iii) *An Enlarged Sprue Base.*<sup>5-9, 10-13</sup> This should allow the change in direction and reduction in velocity of the stream to occur with little agitation or erosion, but must generally be small enough to be filled without "spoiling" a large volume of metal by entrainment of the displaced air. The best shape has yet to be determined, but satisfactory results have been obtained with a cylindrical enlargement having a horizontal cross-section about five times that of the sprue exit and a depth twice that of the runners;<sup>8</sup> these are best taken off the top half of the sprue base, as in Fig. 1 (p. 268). A large rectangular enlargement or "surge sump" may also be used, the runners being uprun from the base to exclude the dross formed in filling the sump<sup>13</sup> (Fig. 4, p. 269).

#### (c) The Runner

If the cross-section of the runner near the sprue base is too large, the stream of metal leaving the sprue incompletely fills the runner, and oxidation of the top surface of the stream can readily occur, possibly accompanied by agitation, local aspiration, and entrainment of air. This tendency is, of course, accentuated by a badly designed sprue base, e.g. one excessively choked, which delivers metal at too great a velocity.

The stream of metal widens as friction along the horizontal runner causes the velocity to fall (the rate of flow past successive points along the runner being constant under steady conditions), and the metal may eventually



fill the cross-section of the runner.<sup>5, 14</sup> Agitated flow of oxidized metal into the mould cavity is thus discouraged by the use of a long runner which steadily chokes the stream; slight uprunning of the mould or gating off the top surface of the runner<sup>12</sup> also results in rapid filling of this channel. Alternatively, oxide on the surface of the stream is said to be prevented from entering the casting, even if the runner is only partly filled, by gating-off the bottom of the runner.

Clearly all these precautions can be made effective if properly applied, but whatever method is adopted to cause the runner eventually to fill, some of the inclusions introduced earlier near the base of the sprue are likely to remain.<sup>5</sup> Even a well-designed sprue must therefore be connected with a runner of the correct dimensions if the effects of agitation are to be avoided completely. The

consist of a wire mesh, a pad of wire wool, or a perforated biscuit-core, placed across the metal stream near the base of the sprue.<sup>15</sup> Some at least of these devices filter oxide from the metal, but most of their beneficial effect appears to be due rather to their choking action, which ensures that the sprue system is filled.<sup>6, 7</sup> It is hardly surprising, therefore, that further drossing or air entrapment may occur beyond the filter if it is not sited correctly;<sup>1</sup> such defects are probably least likely when both sides of the filter are completely covered by metal, e.g. if the stream is made to rise through a horizontal filter.<sup>16</sup> It is doubtful, however, whether a filter is ever more effective than a well-designed running system alone, particularly as the holes in many forms of filter are of necessity too large to hold back all harmful dross particles. The advantages of this form of trap are that it may increase the casting

TABLE I.—Dimensions and Flow Rates Through Tapered Sprues.

3-in.-deep pouring basin

Sprue Exit Dia., in.	Sprue Entry Dia., in.						Approx. Flow Rate Through Lightly Choked or Unchoked System, in. <sup>3</sup> /sec.					
	6-in. sprue	9-in. sprue	12-in. sprue	18-in. sprue	24-in. sprue	48-in. sprue	6-in. sprue	9-in. sprue	12-in. sprue	18-in. sprue	24-in. sprue	48-in. sprue
$\frac{1}{4}$	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{7}{16}$	...	...	...	4	5	5	...	...	...
$\frac{3}{8}$	$\frac{9}{16}$	$\frac{9}{16}$	$\frac{5}{8}$	$\frac{5}{8}$	...	...	9	11	12	14	...	...
$\frac{1}{2}$	$\frac{11}{16}$	$\frac{3}{4}$	$\frac{13}{16}$	$\frac{7}{8}$	$1\frac{1}{16}$	...	16	19	21	25	28	...
$\frac{5}{8}$	$\frac{7}{8}$	$\frac{15}{16}$	1	$1\frac{1}{16}$	$1\frac{1}{8}$	$1\frac{3}{8}$	26	30	33	39	44	61
$\frac{3}{4}$	$1\frac{1}{16}$	$1\frac{1}{8}$	$1\frac{9}{16}$	$1\frac{5}{16}$	$1\frac{3}{8}$	$1\frac{5}{8}$	37	43	48	56	64	88
1	...	...	$1\frac{9}{16}$	$1\frac{11}{16}$	$1\frac{13}{16}$	$2\frac{1}{8}$	...	...	85	100	110	160
1.5	...	...	...	$2\frac{3}{8}$	$2\frac{11}{16}$	$3\frac{1}{8}$	...	...	...	150	170	230

cross-section of the runner required cannot be specified in terms of the sprue diameter alone, as it also depends on the reduction in metal velocity achieved in the sprue base and on the sizes of the gates; the relative sizes of runners and sprues are discussed further in the description (p. 268) of gating systems. The most satisfactory shape is probably an inverse-tapered runner, slightly uprun,<sup>1, 13</sup> but excellent results have also been obtained with parallel runners, as described below. However, sharp bends and sudden changes in cross-section should be avoided, as they may result in the formation of "dead" pockets, causing agitation and the entrainment of air.<sup>6</sup>

#### (d) Dross Traps

Dross traps may be used either: (i) to divert the first-poured metal, which is inevitably contaminated with dross formed while the running system is being filled, or (ii) to remove dross which is continually formed in an imperfectly designed gating system. The first function is adequately performed by a simple extension to the runner which passes beyond the final gate, preferably to a sump; the momentum of the first-poured metal carries it into the sump before any metal enters the gates, provided these are taken off the top or side of the runner. As the sump represents a loss of metal, the minimum size should be determined for each running system.<sup>12</sup>

Traps which filter dross from the metal stream usually

yield by simplifying the running system and can also be used to facilitate "knock-off".

A serrated top surface and other forms of projection on the runners have also been advocated as dross traps,<sup>17</sup> but these shapes probably have little advantage over a plane surface in holding back oxide floating on the stream, if the runners are completely filled.

#### (e) The Gates and the Gating Ratio

Castings in dross-forming alloys are preferably gated near the base to prevent metal splashing into the mould cavity; the back pressure of metal in the mould as it fills helps to keep the runners full. Agitation and entrainment of air are likely to occur near the junction of the gate with the runner, if the angle between them is sharp, but may be greatly diminished by streamlining the junction, and simultaneously reducing the cross-section of the runner to avoid enlargement of the total cross-section of the channels.<sup>12</sup>

Multiple-gate systems are often used to produce an even temperature distribution in the casting, particularly to avoid local hot spots which give rise to shrinkage hot tears and distortion. It is difficult to achieve uniform flow throughout a multiple-gate system, however, as the momentum of the metal carries the largest proportion of the stream through the gates remote from the sprue; indeed, too great a momentum may even cause the

flow of metal to be reversed through gates near the sprue.<sup>18</sup> Observation of the performance of varied arrangements of gates<sup>19</sup> indicates that uniform flow is encouraged by: (i) reducing the momentum of the stream by the employment of enlarged runners, (ii) increasing the resistance to flow through the end gates by suitably reducing their cross-section and/or that of the runner, thus raising the pressure at the other gates, or (iii) distributing the momentum of the stream more evenly by varying the angles between the arms of the runner and the gates. The first two methods are the most generally applicable, but the relative dimensions of the runners and gates and their relation to those of the sprue are critical.

The ratio of the total cross-sections of the sprue, runners, and gates is known as the gating ratio and is expressed in the form  $x : y : z$ . This quantity is of great importance in the performance of a running system because, as explained above in discussing the individual features of the system, the gating ratio determines: (i) the uniformity of flow in a multiple-gate system, (ii) the degree of agitation, erosion, and aspiration between the sprue and the casting, (iii) the velocity at which the metal is delivered into the mould cavity and hence the extent of drossing and erosion there, and (iv) the total rate of flow.

Unfortunately, the criteria used by different workers to assess the performance of a running system are so varied that the gating ratios recommended cover a considerable range, but the results discussed by Ruddle<sup>1</sup> and summarized in Table II suggest that the ratios listed in the final column of the table are probably the most satisfactory.

TABLE II.—Recommended Gating Ratios.

Metal	Range of Recommended Ratios (approx.)	Probably Most Suitable Ratios
Steel	10 : 8 : 6 to 1 : 2 : 2	1 : 2 : 2 to 2 : 2 : 1
Cast Iron	4 : 3 : 1 to 1 : 1 : 1	2 : 2 : 1
Gun-metals and bronzes	(Castings little affected by gating ratio)	Probably 1 : 2 : 1 to 2 : 2 : 1
Aluminium bronze	1 : 3 : 5	1 : 4 : 4 to 1 : 6 : 6 with (i) gates from the top of the runner or (ii) up-running; or 1 : 4 : 3 to 1 : 6 : 4 with gates attached to side or bottom of the runner and without up-running.
High-tensile brass	1 : 2 : 1 to 1 : 3 : 5	
Aluminium alloys	4 : 4 : 3 to 1 : 6 : 6	
Magnesium alloys	1 : 2 : 2 to 1 : 4 : 4	

The most highly choked (i.e. "pressurized") systems are probably to be preferred for alloys such as phosphor-bronze and gun-metals, because, while considerable agitation may be tolerated, advantage can be taken of the simplicity—and hence the high casting yield—of choked systems, the easier attainment of uniformity of flow when used with multiple gates, and the ease of control of pouring; care must be taken, however, to avoid mould erosion due to high metal velocities. For alloys which form oxide skins, on the other hand, the avoidance of aspiration and agitation is of paramount importance, and "unpressurized" systems with high gating ratios \*

are therefore to be preferred; in such cases, however: (i) careful attention must be given to the relative dimensions of gates and runners to achieve the correct flow through each gate, (ii) some precaution such as up-running must be taken to ensure filling of the large runners and gates, (iii) the rate of pouring should be checked to ensure that the lightly choked sprue is filled, and (iv) rather high moulding and metal-handling costs would usually be incurred owing to the complexity of the running and gating systems.

#### (f) Integrated Horizontal Running Systems

A number of horizontal running and gating systems have been devised which have given satisfactory results with the particular castings and alloys studied; these systems have been considered elsewhere.<sup>1</sup> Lack of space

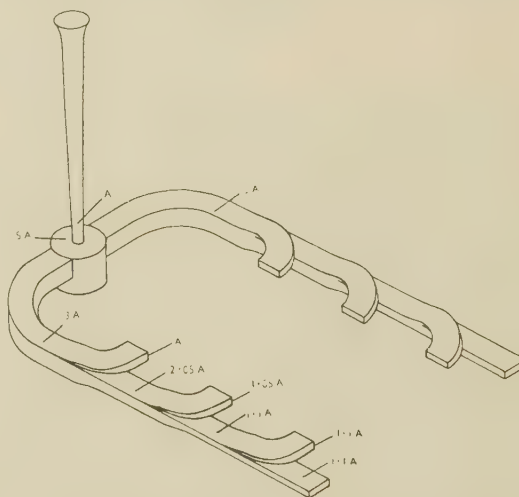


Fig. 1.—Running System Based on That Developed by Eastwood *et al.* Gating ratio approx. 1 : 6 : 6. Cross-sectional areas are indicated.

precludes discussion here of more than two, but each embodies several of the features recommended in previous sub-sections and appears to be particularly worthy of application when greater control of the running and gating is required for castings in a dross-forming alloy.

The system illustrated in Fig. 1, based on that devised by Eastwood and his co-workers,<sup>8,12</sup> is an unchoked system of gating ratio about 1 : 6 : 6, with a tapered sprue leading to a well-base and gates taken off the top of the runners to ensure filling. The carefully chosen dimensions of the gates and the large stepped runner maintain uniformity of flow by reducing the momentum of the stream and balancing the resistance to flow through the several gates, as discussed above (Sub-section (e)). Several workers have used this type of system successfully.<sup>1</sup> Simplified versions of the system applied to a cylinder and a plate, shown in Figs. 2 and 3, respectively, have also proved satisfactory.<sup>20</sup>

The second running system, illustrated in Fig. 4, is based on one recommended by Robertson and Hardy,<sup>13</sup> but has a tapered sprue instead of the original cylindrical sprue. This system is also one of high gating ratio (approx. 1 : 4 : 6), but the gates are choked at their junctions with the runner to pressurize the sprue and

\* A high gating ratio is here defined as one in which the gate area considerably exceeds the sprue area.



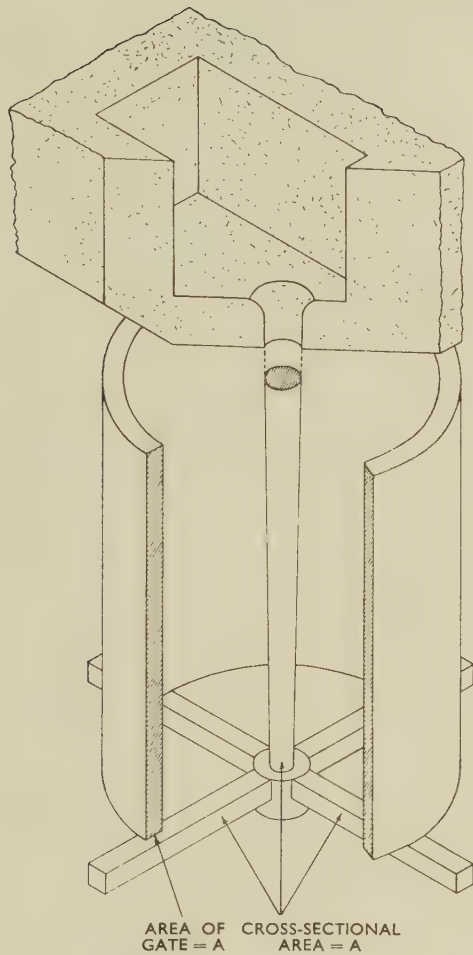


FIG. 2.—Application of a Simplified Version of Eastwood Running System to a Hollow Cylindrical Casting (diagrammatic). Gating ratio 1 : 4 : 4. Cross-sectional areas are indicated.

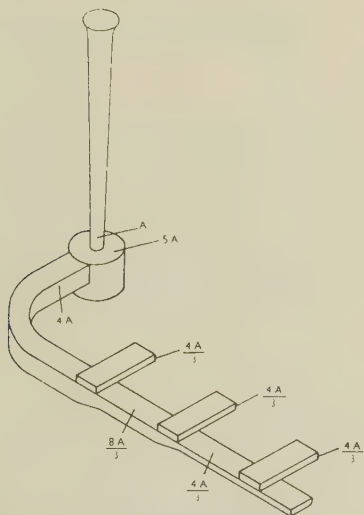


FIG. 3.—Application of Simplified Version of Eastwood Running System to a Plate Casting (diagrammatic). Gating ratio 1 : 4 : 4. Cross-sectional areas are indicated.

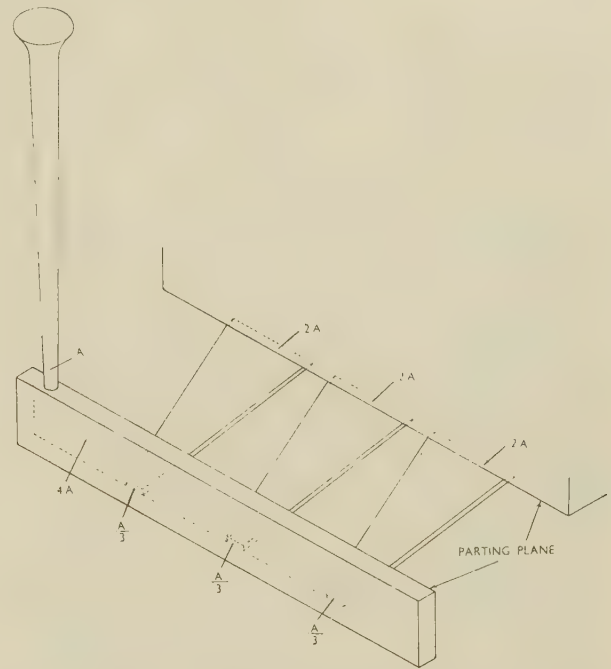


FIG. 4.—Running System Based on That Developed by Robertson and Hardy, but Including a Tapered Sprue. Gating ratio approx. 1 : 4 : 6. Cross-sectional areas are indicated.

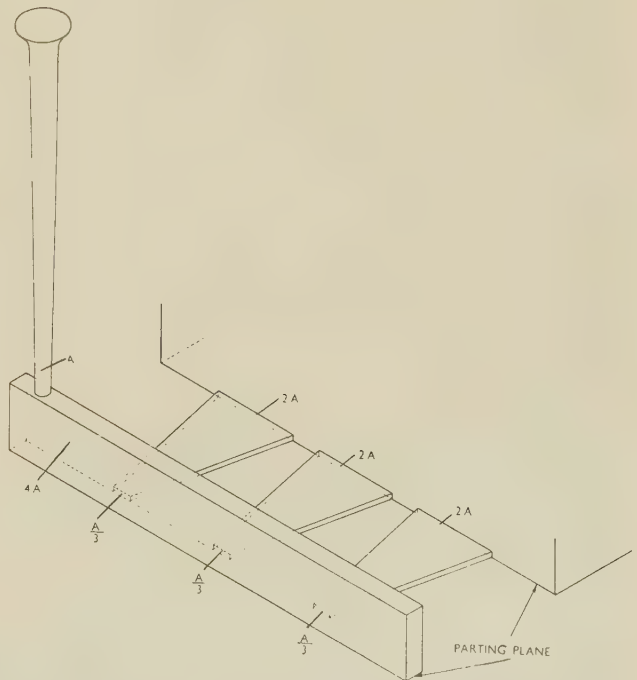


FIG. 5.—Modified Version of Running System Developed by Robertson and Hardy. Gating ratio 1 : 4 : 6. This system is intended to be uprun. Cross-sectional areas are indicated.

runner and to encourage uniform flow; agitation due to rapid flow through the entrances of the gates is prevented by their inverse taper and upward incline. A similar but more easily moulded system is shown in Fig. 5, the necessary inclination of the gates being obtained by uprunning the casting.

#### (g) Vertical Gating Systems

Although bottom gating is often employed for dross-forming alloys, use being made of one of the horizontal gating systems already described, the unfavourable temperature gradients induced in certain castings may create difficulties in feeding. For such castings (vertical) stepped gating systems have been advocated, but in the simple forms metal may not flow through the successive gates in the correct sequence and may even permit reverse flow, owing to momentum effects. The results of measurements of flow rates in more satisfactory, but complicated forms devised by Johnson, Baker and Pellini<sup>18</sup> have been summarized elsewhere.<sup>1</sup>

An alternative method of overcoming the effects of the unfavourable temperature gradients created by bottom gating has been advocated by Grube and Kura.<sup>21</sup> These workers recommend bottom gating into a vertical feeder which is connected with the casting through a continuous slot gate up the side of the feeder; the dimensions of the slot are such that it does not freeze before the casting, and adequate feeding can therefore take place.

#### (h) Rate of Flow

The rate of flow into the mould cavity depends on the resistance offered by each part of the running and gating system and is not simply a function of the sprue dimensions.<sup>1</sup> If the effects of friction and turbulence are neglected and the mould cavity is assumed well vented, the velocity and rate of flow can be calculated from: (i) Bernoulli's equation, which states that the sum of the potential energy (due to height and pressure) and the kinetic energy (due to motion) is constant, and (ii) the principle of the continuity of flow, which simply implies that the product of the velocity and cross-sectional area along the stream is constant under steady conditions. In practice, losses of energy due to friction and turbulence occur which are proportional to the kinetic energy, and Bernoulli's equation must therefore be corrected by including terms for such losses; known loss coefficients for the various parts of a running system have been listed elsewhere, with details of the method of calculating flow rates and velocities in single- and multiple-gate systems.<sup>1</sup>

The calculation of flow rate is greatly simplified if the running system is not choked beyond the sprue base and the metal velocity (and hence, energy losses) in the runners and gates is low. It can then be assumed, with sufficient accuracy for many purposes, that the flow is controlled mainly by the area of the sprue exit and the height of metal above it, i.e.:

$$W = w A \sqrt{2gh} \quad (2)$$

where  $W$  = flow rate (lb./sec.),  $w$  = specific weight of metal (lb./in.<sup>3</sup>),  $A$  = area of sprue exit (in.<sup>2</sup>),  $h$  = height of metal in sprue and pouring basin (in.),  $g$  = gravitational constant.

Figures calculated in this way have been included in

Table I, from which sprue dimensions which allow a casting of given weight to be filled in a convenient time can easily be determined.

## 2. THE FILLING OF THE MOULD CAVITY

If the gating system is such that metal enters the mould cavity quietly without dross, the principal defects likely to arise in the mould (apart from those due to poor sand condition and ramming) are incomplete filling of thin sections and poor reproduction of detail such as sharp corners.

Lack of detail may be due to premature solidification caused by the use of too low a casting temperature. Fidelity of reproduction is generally poorest in alloys on which tenacious oxide films are formed and the apparent surface tension of which is therefore high; conversely, sharper detail is obtainable by the addition of an element such as phosphorus to copper, which prevents the formation of solid oxide scales, but the greater power of penetration may, of course, lead to poorer surface finish owing to the entry of metal into flaws in the mould surface, particularly at the bottom of the casting.

Casting fluidity, or the ability of an alloy to flow through thin sections, is generally assessed by the length of run in a channel moulded under standardized conditions. Although spiral forms are most frequently used, as they accommodate great lengths easily, it is doubtful whether they provide more useful information than can be obtained from straight channels, which can probably be moulded more simply and reproducibly.<sup>22, 23</sup> A properly designed running system leading to the channel is essential to secure consistency of results in a foundry fluidity test.

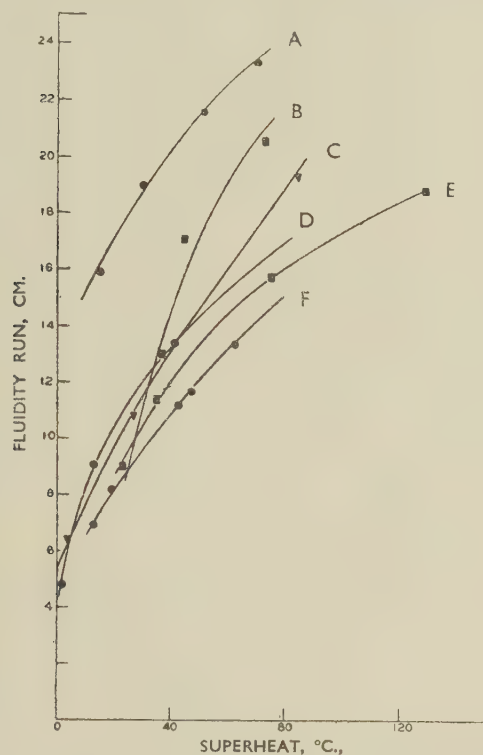
As the distance through which the metal can flow is limited by the time available before the channel becomes clogged by partial solidification, the heat content of the metal (i.e. its superheat, density, and specific heat) and the chilling properties of the mould are important factors controlling fluidity. In practice, this means that the use of a higher pouring temperature is a simple way of improving fluidity, as illustrated by the results for a few aluminium alloys in Fig. 6.<sup>24</sup> Increasing the mould temperature has a similar effect, if the difference between this temperature and the freezing point of the alloy is significantly reduced.<sup>22</sup>

An increase in the velocity of metal entering the mould cavity should also prolong the flow. Raising the height of the pouring basin, for example, increases metal velocity in certain running systems, while adequate venting has a similar effect, since it prevents the development of back pressure. In comparison with the forces causing flow due to the head of metal in the system, the opposing surface-tension forces are negligible except in very narrow channels;<sup>25</sup> surface tension probably has little influence on fluidity generally, therefore, in spite of its considerable effect on surface detail.

The fluidity of a series of alloys varies greatly with composition, being high for a pure metal and a eutectic, for example, and tending to fall to a minimum at a composition between these.<sup>22, 26</sup> The reasons for this variation with composition are uncertain, but two may be suggested. The temperature of the metal entering the mould falls rapidly to the liquidus temperature, but thereafter drops more slowly because the latent heat of



freezing is large in comparison with the specific heat and the chilling power of the mould declines steadily. Consequently, solidification may begin long before the flow of metal ceases, and it is feasible that the length of flow is



[Courtesy Institute of British Foundrymen.]

FIG. 6.—Effect of Superheat on Fluidity of Various Aluminium Alloys. (Lees.<sup>24</sup>)

#### KEY

- Curve A. Commercial aluminium (f.p. 657° C.).  
 " B. Al-Si eutectic (liquidus taken as 577° C.).  
 " C. Cu 2-0, Si 2-0 (liquidus 643° C.).  
 " D. Cu 2-0, Si 0-25 (liquidus 653° C.).  
 " E. Cu 2-0, Si 5-0 (liquidus 621° C.).  
 " F. Cu 6-8 (liquidus 632° C.).

affected by the mode of solidification: in particular, the shell of solid metal in skin-forming alloys, i.e. pure metals and certain eutectics, would probably retard the flow of the remaining liquid much less effectively than the dispersed equiaxial dendrites in pasty alloys of intermediate compositions. This order of effect is consistent with the variation in fluidity described above. However, Kondic and his co-workers<sup>22, 26</sup> question the significance of such an effect and suggest that the variation in viscosity of the liquid metal with composition suffices to explain the similar changes in casting fluidity. The results of viscosity determinations so far available, however, are not considered by the present authors to be conclusive.

### III.—MECHANISM OF FREEZING: HEAT FLOW IN CASTINGS

#### 1. MODE OF FREEZING

In discussing the mode of freezing, it is convenient to divide metals and alloys into three groups:

(1) Pure metals and certain alloys of short freezing range.

(2) Solid-solution alloys of moderate and long freezing range.

(3) Eutectics.

The way in which materials in each of these groups freeze is briefly discussed below.

#### (a) Freezing of Pure Metals

When a pure metal is poured into a mould, solidification begins by the deposition of a layer of crystallites on the mould walls. The more favourably oriented crystallites grow perpendicularly to the mould wall, advancing into the liquid interior of the casting and joining up to form a solidification front, as illustrated in Fig. 7. Solidification continues by the further growth of these crystals, the front advancing towards the centre of the casting until it meets the front which will meanwhile have advanced from the other side, thus completing the solidification of the casting. This mode of freezing, in which the casting consists of a liquid core surrounded by a solid shell, is known as "skin-formation" and strictly speaking occurs only in pure metals and possibly in certain eutectic alloys<sup>27</sup> (see below). Because freezing in pure-metal castings proceeds by the growth of crystals attached to the mould walls, the macrostructure is almost completely columnar.

However, a closely similar mode of freezing occurs in certain alloys of short freezing range, the solidification front, in this case, being a narrow band instead of a plane interface, the boundaries of which correspond with the positions of the liquidus and solidus isotherms. An important example of this class of material is low-carbon steel, which for some practical purposes may be

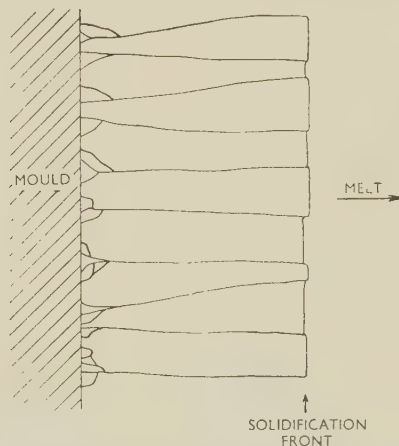


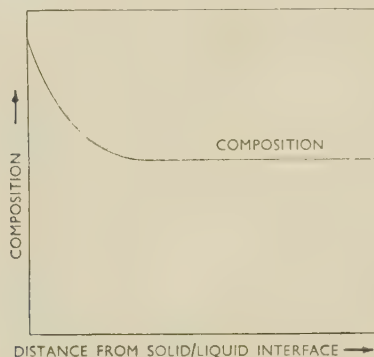
FIG. 7.—Mode of Solidification of a Pure Metal.

regarded as freezing by skin formation. The width of the band of partial freezing depends on the alloy system and on the freezing range, increasing rapidly with the latter. For this reason many alloys of quite moderate freezing range, such as high-carbon steel and 60 : 40 brass, and even 99% pure aluminium, cannot justifiably be regarded as freezing by skin formation. The closeness with which solidification in an alloy of short freezing range approaches that of a pure metal increases with increase in the rate of cooling, so that many materials which do not behave like a pure metal when sand cast appear to do so when they are chill cast. High-carbon

steels form one example and some aluminium alloys another.

### (b) Freezing of Solid-Solution Alloys

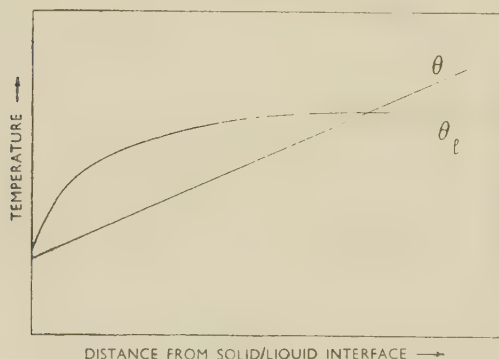
In these materials, too, freezing begins by the deposition of crystallites on the mould walls. However, because these crystallites will normally contain less solute than the melt, the immediately adjacent liquid becomes enriched in solute, as indicated in Fig. 8.<sup>28-31</sup> This



[Courtesy American Institute of Mining and Metallurgical Engineers.]

FIG. 8.—Concentration of Solute in Liquid Surrounding Growing Crystallites. (Chalmers.<sup>31</sup>)

enriched layer of liquid adjacent to the first-formed crystallites cannot diffuse away rapidly enough to maintain equilibrium, even in slowly cooled castings. Growth of the first-formed crystallites cannot proceed unless their temperature keeps pace with the change in the freezing point of the surrounding liquid; <sup>30, 31</sup> liberation



[Courtesy American Institute of Mining and Metallurgical Engineers.]

FIG. 9.—Constitutional Supercooling During Freezing of an Alloy. The line  $\theta_l$  shows how the freezing point of the liquid surrounding a crystallite varies with distance; the line  $\theta$  indicates the temperature gradient in the liquid. (Chalmers.<sup>31</sup>)

of latent heat of fusion tends to prevent this. The temperature near the mould walls nevertheless falls a few degrees, and this produces a temperature gradient uphill towards the interior of the casting, as shown schematically by the line  $\theta$  in Fig. 9.<sup>31</sup> The line  $\theta_l$  indicates the way in which the freezing point of the liquid near the mould wall varies with distance, in particular that there is a region adjacent to the crystallites at the mould wall in which the temperature of the liquid is below its freezing point, i.e. the liquid is undercooled. This type of under-

cooling has been called by Chalmers<sup>31</sup> "constitutional supercooling" and if the amount is sufficient, nucleation of new crystallites takes place. Growth of this second batch of crystallites is also quickly restricted, and constitutional undercooling again occurs, followed by the nucleation of a third batch of crystallites nearer the centre of the casting. This cycle of events is quickly repeated until crystallites have been nucleated throughout the entire casting. In other words, a wave of undercooling sweeps through the casting from its surface to the centre, nucleating crystallites in the metal through which it passes. Freezing then proceeds by the gradual enlargement of these crystallites, which takes place simultaneously at all locations. The crystallites near the mould walls grow rather faster than those in the centre of the casting, but the difference in rates of growth is not usually large in a sand casting. This type of freezing is exemplified in Fig. 10, which gives cooling curves taken at various points between the surface and centre of a large cylindrical casting.<sup>32</sup> The figure also shows the variation with time of the percentages of solid: (i) at the metal/mould interface, and (ii) at the centre of the casting; the difference in the percentages of solid material never exceeds 20%, and towards the end of freezing becomes very small indeed.

Since freezing in these alloys proceeds at the same time at numerous independent centres throughout the casting, the macrostructure of the solid casting is equiaxial, the fineness of the structure being clearly governed by the number of centres at which freezing takes place. As has been shown by Turnbull and others,<sup>33, 34</sup> a very large amount of undercooling is necessary before spontaneous nucleation takes place in a perfectly pure metal or alloy; the amount of undercooling required for this is about 20% of the freezing temperature of the metal expressed in °K. However, in any real casting, there are inevitably present in the melt tiny particles of oxide and other foreign bodies which facilitate nucleation, permitting it to occur at only a few degrees of undercooling, and it is upon these nuclei that solidification takes place; the number of suitable nuclei is not large, so that relatively few crystallites form within the casting, which therefore solidifies with a coarse equiaxial structure. Clearly, if it were possible to increase the number of nuclei present in the melt at the beginning of the solidification process, many more crystallites would form and a fine equiaxial structure would result. This, in fact, is the theoretical basis of methods of grain refining castings, in which particles capable of nucleating the primary phase at a very small degree of undercooling are introduced into the melt. Cibula has suggested<sup>30, 35-38</sup> that the effectiveness of these nucleants depends upon the extent to which they possess the following physical attributes:

(i) The lattice spacing and structure of the nuclei should be similar to those of the nucleated phase; lattice misfits of up to 20-30% are, however, tolerable in some cases.

(ii) The type of bonding in the nucleating particles must be essentially metallic or ionic in nature.

(iii) The nuclei must be stable, i.e. they must not be decomposed by any of the constituents present in the alloy.

Examples of nuclei used in practice are titanium carbide and titanium boride for aluminium alloys, zirconium carbide or nitride for copper alloys, zirconium for mag-



nesium alloys, and lead sulphide, selenide, or telluride for lead. These nuclei are normally formed in the melt by separately adding their constituent elements (e.g. in aluminium alloys by adding titanium which combines with traces of carbon normally present to precipitate  $TiC$ , or with boron added separately to form  $TiB_2$ ).

In some alloys the amount of constitutional supercooling during freezing is insufficient to promote crystallization at new centres (in the absence of grain-refining

axial one by reducing the amount of constitutional supercooling necessary for solidification at new centres.

Addition of grain refiners to substantially pure metals does *not* normally produce a fine-grained equiaxial structure, because growth of the first-formed crystallites is not restricted by solute enrichment of the surrounding liquid.<sup>30</sup> (However, if some excess of the grain refiner is present in solution, the refiner will itself produce some enrichment near the growing crystallites, which may be

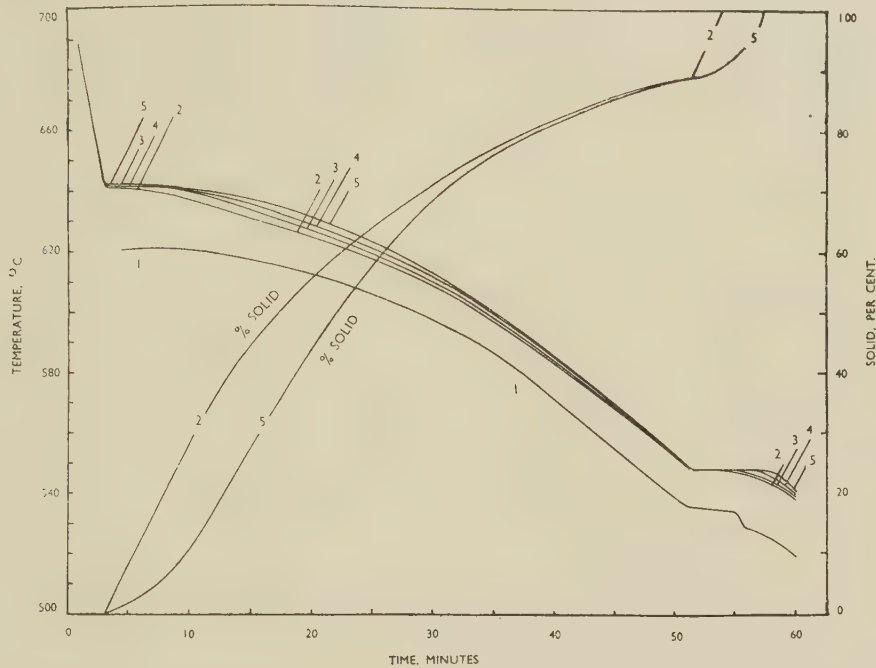


FIG. 10.—Cooling and Percentage-Solid Curves in a Horizontally Cast 5-in.-dia. x 10-in. Cylinder in an Aluminium-4% Copper Alloy.

Positions of thermocouples :

- |                           |                          |
|---------------------------|--------------------------|
| 1. Interface (sand side). | 4. 2 in. from interface. |
| 2. " (metal side).        | 5. 5 in. " "             |
| 3. 1 in. from interface.  |                          |

additions for which the required degree of undercooling is very small), and a mode of freezing occurs which is in some respects intermediate between the freezing of pure metals by skin formation and the pasty mode of freezing of alloys of long freezing range to yield equiaxial structures.<sup>27, 37</sup> In this intermediate type of freezing the crystals deposited on the mould wall are able to grow into the melt. Their growth is, however, considerably restricted, and because of this they are unable to link up to form a continuous solidification front, but instead grow in the dendritic manner indicated in Fig. 11. At an intermediate stage in freezing, the casting thus consists of a number of solid dendrite spines advancing slowly into the liquid interior, there being a large amount of still-liquid material between the arms and branches of the dendrites. Frequently, near the centre of such a casting, the degree of constitutional supercooling becomes sufficient to permit deposition on a few new centres and equiaxial crystals may form there. Addition of grain refiners to materials such as bronzes and gun-metals, which frequently freeze in this manner, converts the columnar or semi-columnar macrostructure of this kind into an equi-

sufficient to cause nucleation within the casting). The grain refiner will, nevertheless, greatly increase the

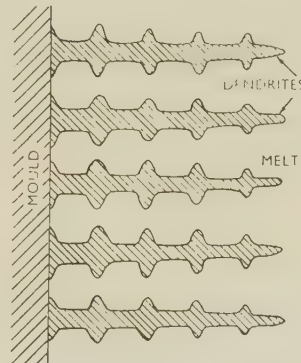


FIG. 11.—Dendritic Columnar Crystal Growth in Alloys.

number of crystallites *formed at the mould wall*, thus refining the columnar structure of the solidified casting.<sup>30</sup> A similar effect can be produced by incorporating a grain refiner in the mould dressing.<sup>39</sup>

## (c) Freezing of Eutectic Alloys

The mechanism of freezing in castings in eutectic alloys has not been studied in such detail and is as yet by no means fully elucidated. Certain alloys of eutectic or near-eutectic composition, such as aluminium bronze, seem to freeze very much like pure metals, skin formation apparently taking place. On the other hand, others, such as the aluminium-silicon eutectic alloys, exhibit many of the characteristics of pasty solidification and during the freezing of these alloys there are often long periods during which almost the entire casting is at the same temperature. The mechanism of heat transfer and freezing in such cases is obscure, but it has been tentatively suggested that heat transfer may take place by movement of solid material.<sup>32, 43</sup>

The total heat absorbed in time  $t$  is given by :

$$Q = 1.128b(\theta_i - \theta_0)\sqrt{t} = \xi\sqrt{t} \quad (4)$$

The quantity  $\xi$  is termed the mould constant and is a measure of the chilling power of the mould.

The applicability of equations (3) and (4) to sand moulds has been demonstrated by several workers.<sup>40, 41</sup> These equations predict that a mould at first absorbs heat from the casting extremely rapidly, but that the rate of heat extraction soon falls off to a relatively modest value, as indicated in Fig. 12, which was obtained experimentally by Ruddle and Mincher.<sup>41</sup> Equations (3) and

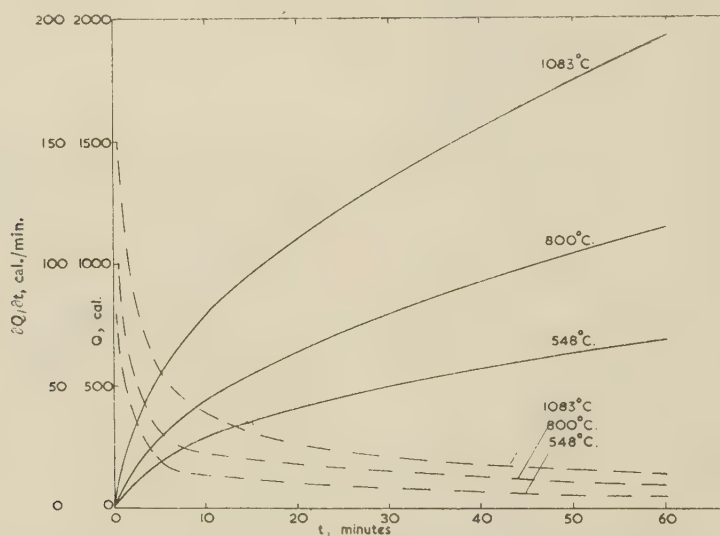


FIG. 12.—Total Heat Extracted  $Q$  and Rate of Heat Extraction  $\partial Q/\partial t$  per cm.<sup>2</sup> of Synthetic Sand Mould Surface for Initial Temperature of 20° C. and Interface Temperatures Indicated.

————— Total heat extracted  $Q$ .

----- Rate of heat extraction  $\partial Q/\partial t$ .

## 2. HEAT EXTRACTION AND FREEZING RATES IN CASTINGS

### (a) Heat Extraction by Moulds

For obvious reasons the rate at which a casting freezes is determined by the rate at which the latent heat of fusion evolved during solidification can be removed by conduction into the mould.\* As has been shown by Chvorinov,<sup>40</sup> Ruddle and Mincher,<sup>41</sup> and others, the rate at which unit area of a plain sand mould extracts heat is given by :

$$\frac{\partial Q}{\partial t} = \frac{0.564(\theta_i - \theta_0)b}{\sqrt{t}} \quad (3)$$

where  $Q$  is the total amount of heat extracted in time  $t$ ,  $\theta_i$  is the temperature of the metal/mould interface (assumed constant throughout solidification),  $\theta_0$  is the initial temperature of the mould, and  $b$  is the heat diffusivity of the mould material and is equal to  $\sqrt{Kc\rho}$  where  $K$  is the thermal conductivity of the mould,  $c$  its mean specific heat, and  $\rho$  its density.

(4) are applicable only to plane mould walls. Heat absorption by curved mould walls and at external corners and edges of castings is more rapid than indicated by these equations. Methods for dealing with this question have been given by Ruddle and Skinner.<sup>42</sup>

It will be noted that according to equations (3) and (4), the mould constant increases with increase in the freezing temperature of the casting. Furthermore, the quantity  $b$  also increases with freezing temperature, since the thermal conductivity of moulding sand rises rapidly with temperature. The cumulative result of these effects is that the mould constant increases markedly with temperature, as shown by the experimental values in Table III.<sup>41</sup>

As indicated by the figures in Table III, green sand extracts heat slightly more quickly than dry sand, but the difference is small. Hard ramming also increases the chilling power of the mould, the effect being quite substantial.<sup>44</sup> Theory and other experimental evidence show that a coarse sand has a lighter chilling power than a fine sand.

\* Radiation to the environment is also involved where the casting or the feeders attached to it have open surfaces.



## (b) Solidification Rates in Castings

Because the absorption of heat by the mould follows a parabolic law (equation (4)), the rate of skin formation also follows a parabolic law, the heat absorbed by the

TABLE III.—Mould Constants for Various Moulding Materials.

Material	Density, g./c.c.	Interface Temp., °C.	Mould Constant, $\xi$ , cal./ cm. <sup>2</sup> /min. <sup>1/2</sup>	Mould Constant Relative to Syn- thetic Sand at 548° C. Interface Temp.
Dry Synthetic Sand (Erith Washed Silica- 5% Bentonite)	1.49	548	89.4	1
		798	151	1.69
		1083	244-260	2.82
Dry Naturally Bonded Sand (Mansfield Red)	1.56	548	93.6	1.05
		1083	228	2.55
Cement-Bonded Sand (Leighton Buzzard No. 52)	1.67	1083	330	3.69
Dry Silicon Carbide (Bonded with 5% Bentonite)	1.95	548	119	1.33
		798	232	2.60
		1083	330	3.69
Green Synthetic Sand	1.54	548	108	1.21
		1083	258	2.86
Green Naturally Bonded Sand	1.64	548	105	1.17
		1083	237	2.65

mould being balanced by the heat of fusion liberated during freezing. Hence,  $d$ , the depth of metal frozen in a given time  $t$ , is given by:

$$d = q\sqrt{t} \quad (5)$$

where  $q$  is the "solidification constant" and is given by:

$$q = \frac{1.128b(\theta_i - \theta_0)}{L\rho'} \quad (6)$$

In this equation  $L$  is the latent heat of fusion and  $\rho'$  is the density of the metal at the freezing point.<sup>27, 40, 43</sup> Equations (5) and (6) assume that the casting is poured without superheat, but in fact it has been shown<sup>40, 43</sup> that the existence of superheat merely adds a constant to equation (5), which then becomes:

$$d = q\sqrt{t} - c \quad (7)$$

A few experimental values of  $q$  and  $c$  for non-ferrous metals freezing against a plane mould wall are given in Table IV;<sup>43</sup> in all cases the metal was poured with a superheat of 100° C.

It is interesting to note from Table IV that aluminium and copper freeze at about the same rate in a given type of sand mould; although the mould constant is higher for a copper casting, this is counterbalanced by the fact that the latent heat *per unit volume* is much greater for copper than for aluminium. On the other hand, magnesium freezes faster than aluminium (despite almost identical mould constants) because its latent heat *per unit volume* is considerably smaller than that of aluminium.

Equations (5)–(7) are true only for the case of a plane mould wall, and care must be taken in applying these equations to castings of complex shape. Equation (7) may be used to compute the progress of solidification from points near the centre of the large faces of a plate whose length and breadth are large compared with the thickness, and will be found to hold good right to the end

TABLE IV.—Solidification Constants for Non-Ferrous Metals.

Metal or Alloy	$q$ , in./min. <sup>1/2</sup>	$c$ , in.	Approx. Volume Latent Heat ( $L\rho'$ ), cal./cm. <sup>3</sup>
Aluminium . . . .	0.26	0.29	242
Copper . . . . .	0.27	0.18	405
Magnesium . . . .	0.50	0.65	147
Zinc . . . . .	0.23	0.45	164
Copper-10% Aluminium .	0.27	0.27	380

of freezing. On the other hand, in castings such as cubes, where the length and breadth are similar to the thickness, the solidification front must be regarded as three-dimensional, and it must be realized that as solidification proceeds the area of the front contracts.<sup>27</sup> Since the latent heat of fusion liberated at the front is being removed by a constant area of mould wall, the front will tend to move faster in such a case than is predicted by the parabolic law. Furthermore, in castings of this shape the rate of heat extraction at the edges and corners is higher than at the plane mould walls, and this will also tend to cause departures from the parabolic law in the direction of higher rates of freezing. Cylindrical mould walls remove heat faster than plane mould walls, and where they exist the parabolic law will not hold.<sup>42</sup> At re-entrant corners and edges of castings, the rate of heat extraction is, however, much the same as at a plane mould wall.<sup>42</sup>

Because in alloys of long freezing range there is no true solidification front or even a band of solidification, it is impossible to apply skin-formation calculations of the kind discussed above to the freezing of such materials, and all that can be done in the way of computing freezing rates is to calculate the time at which the castings become fully solid. This can be done by equating the heat absorbed by the mould (equation (4)) with the amount of heat which must be liberated by the entire casting during its freezing.<sup>27</sup> The following equation is thus obtained for the time of complete freezing:

$$\sqrt{t} = \frac{\rho' V [L + S(\theta_c - \theta_i)]}{1.128 A b (\theta_i - \theta_0)} \quad (8)$$

where:

- $A$  = surface area of the casting,
- $V$  = volume of the casting,
- $L$  = latent heat of fusion of the alloy,
- $S$  = mean specific heat between the casting temperature and the mean freezing temperature,
- $\theta_c$  = the casting temperature.

This equation is strictly applicable only to castings in which corner and surface-curvature effects are negligible and is therefore likely to be somewhat in error when applied to real castings; the error will be in the direction

of too long time and will increase with decrease in the size of the casting. This equation is, of course, equally applicable to materials which freeze by skin formation. It will be noted that the equation predicts that:

$$t = \text{const.} \times \left(\frac{V}{A}\right)^2 \quad \dots \quad (9)$$

so provided that the mould material, the pouring temperature, and the metal cast are held constant, the freezing time of a casting should be proportional to the ratio  $\left(\frac{V}{A}\right)^2$ . This is the well-known Chvorinov rule,<sup>40</sup> and although for reasons given above it is only approximate, it has nevertheless proved of great value. The constant in Chvorinov's equation depends upon the metal, pouring temperature, and mould material, but is about 20 for copper alloys, 17 for aluminium alloys, and 8 for magnesium alloys, when the units are inches and minutes. A more detailed treatment of this subject has been given elsewhere by one of the authors.<sup>27</sup>

### 3. MODE OF FREEZING AND FEEDING PRACTICE

#### (a) Types of Shrinkage Porosity

During freezing of a casting the metal in the mould cavity decreases in volume by 3–9% (generally about 5–6%), depending upon the alloy in which the casting is made.\* Therefore, unless liquid metal is supplied to the casting to compensate for this volume change, the casting will: (a) contain internal cavities, or (b) fail to occupy the whole volume of the mould cavity at the completion of solidification.

Before considering the way in which the shrinkage that takes place during the freezing of a casting can best be compensated, it is pertinent to consider how the mode of freezing affects the nature of this shrinkage. In the case of alloys which solidify by skin formation, the feeding shrinkage generally takes the form of an axial pipe either open at the top of the casting (i.e. in the feeder) or completely hidden within the casting (secondary pipe, often called centre-line shrinkage). The latter type often consists of a chain of moderate-sized cavities rather than a true pipe. In addition, quite large cavities roughly spherical in shape may be present at isolated heat centres. The essential features of shrinkage cavities in these alloys is that they are concentrated in the last parts of the casting to freeze and are large by comparison with the cavities present in castings in alloys of long freezing range.

In this latter class of alloy, which solidifies in the pasty manner, freezing is taking place concurrently virtually throughout the entire casting, and all the growing crystallites are competing at the same time for the residual liquid present; shrinkage porosity therefore generally takes the form of numerous small cavities scattered throughout the casting. This type—known as microporosity—is dispersed porosity in which the cavities are discrete or interconnected; the latter is, for obvious reasons, the most harmful. The alloys which solidify in the intermediate dendritic fashion described above (Fig. 11, p. 273) tend to show both a certain amount of dispersed porosity and larger cavities concentrated in the central regions of the casting. The size

and the shape of the dispersed cavities formed in long-freezing-range alloys often depend upon the grain-size (see Section IV. 2, p. 286).

Castings in certain alloys of long freezing range exhibit a particularly damaging form of microporosity known as "layer" porosity when fine-grained, the small shrinkage cavities being arranged in numerous layers; the individual cavities tend to be interconnected. The layers are generally perpendicular to the direction of heat flow during freezing, although in certain alloys of exceptionally fine grain (e.g. magnesium alloys containing zirconium) they may be parallel to the direction of heat flow. As shown by Baker,<sup>46</sup> Jay and Cibula,<sup>47</sup> Cibula,<sup>37</sup> and others, this kind of porosity greatly affects the strength and especially the ductility of the casting. The principal alloys in which layer porosity is found are magnesium alloys, aluminium–10% magnesium alloy, and tin bronzes and gun-metals. A mysterious feature of this kind of porosity is that it appears only in certain alloys (e.g. aluminium–10% magnesium alloy), being never observed in other closely similar alloys (e.g. aluminium–4½% copper alloy).

Alloys of the first group (i.e. those which pipe) are sometimes known as "high-shrinkage" alloys, the alloys of long freezing range which constitute the second group being referred to as "low-shrinkage" alloys. These terms are misnomers and have evidently arisen because shrinkage cavities are larger and much more obvious in castings of alloys of the first group. Alloys of the first group do not in fact have larger solidification contractions than those of the second group; often the reverse is the case (e.g. the "low-shrinkage" 85:5:5:5 leaded gun-metal has a solidification contraction of about 6%, whereas that of 90:10 aluminium bronze, a "high-shrinkage" alloy, is only about 4%).<sup>45</sup>

#### (b) General Principles of Feeding Practice

##### (i) The Forces Promoting Feeding

Feeding is normally effected by attaching to the casting a relatively large lump of metal known as a "riser" or "feeder" which freezes less quickly than the casting proper and which therefore provides a reservoir of molten metal which can be used to compensate for the shrinkage of the casting. Several forces may cause the molten metal in the feeder to flow into the regions of the casting where shrinkage would otherwise occur. Gravity is obviously one such force, but it must be realized that in the later stages of freezing, passage of feeding metal into the casting may not be easy owing to the small and tortuous channels down which the liquid must flow, so that gravitational forces may not be sufficient. However, a more powerful force can also operate, namely atmospheric pressure.

Considering first "skin-forming" alloys, the walls of the casting will be solid and impermeable at an early stage in freezing, so that any tendency for cavities to develop within the casting will be opposed by a force of 15 lb./in.<sup>2</sup> acting on the surface of the liquid metal in the feeder. This point was clearly appreciated by Taylor and Rominski<sup>48</sup> in developing the use of blind feeders. Because there is no exposed liquid-metal surface on these feeders on which atmospheric pressure can operate,

\* A few alloys, such as those containing substantial amounts of bismuth and grey cast irons, are exceptional in that they undergo little or no contraction on freezing.



it is necessary, for their correct functioning, to insert a small core or other device which permits atmospheric pressure to act on the liquid metal in the interior of the feeder. A recent invention<sup>49</sup> involves placing a capsule containing a gas-generating substance in the top of a blind feeder; when the molten metal fires the capsule, the evolved gas forces liquid into the casting under a pressure substantially higher than atmospheric. Capillary forces in the interdendritic channels down which the feeding liquid flows may also promote feeding, but these forces are likely to be small except at a very late stage in freezing (i.e. when the channels are very small).

The remarks in the last paragraph apply principally to castings in alloys which freeze by skin formation, and require some modification when alloys freezing in the pasty manner are considered. In the first place, atmospheric pressure has a different influence because the walls of the casting are not usually rigid until a late stage in freezing. Atmospheric pressure therefore tends to compress the pasty mass on all sides, thereby promoting "mass feeding" (see below); this may cause the walls of the casting to cave in, thus giving rise to surface sinks (or local surface shrinks at hot spots). Hydrostatic pressure due to gravity has a similar effect in compacting the metal but opposes the caving-in of the walls of the casting. Because the feeding channels in alloys of this class are very fine towards the end of freezing, it is probable that capillary forces play a larger part in feeding than they do in the case of alloys freezing by "skin formation".

#### (ii) *Alloys Freezing by Skin Formation*

Avoidance of shrinkage cavities is in principle relatively simple in alloys of this class, it being necessary only to position the gates, feeders, and chills in such a way that solidification proceeds most rapidly in the thinnest sections of the castings and least rapidly in the thick sections to which are attached heavy feeders. Residual liquid in the intermediate sections then feeds the solidification contraction of the thin sections, the residual liquid in the heavy sections feeds the intermediate sections, and the liquid in the feeder feeds the shrinkage in the heavy sections. (The feeder-metal requirement of the heavy sections is, of course, a composite of the shrinkage in the heavy section itself, plus the shrinkage which took place in the intermediate and thin sections). In this way all the shrinkage cavities are chased into the feeder heads and the casting itself is sound. Some difficulty may be occasioned where there are long uniform sections in which centre-line shrinkage may occur unless special steps, discussed further below, are taken.

#### (iii) *Long-Freezing-Range Alloys*

In alloys of long freezing range the problem of avoiding shrinkage cavities is much more difficult. The reason is not far to seek when one considers the picture of freezing described above, in which all parts of the casting are competing at the same time for the residual liquid, together with the fact that for liquid to reach the outermost parts of the casting from the feeder it must travel down tortuous channels between the freezing dendrites. This picture suggests that it must be extremely difficult to secure complete soundness in castings of this kind and indeed this is found to be the case. The situation is, however, slightly improved by the occurrence of a second

method of feeding in which movement of the pasty mass of solid and liquid takes place ("mass feeding"). This movement is a settling process in which the forces producing settling are: (i) the atmospheric pressure acting on the walls of the casting and feeder, and (ii) gravity. Some evidence suggests that mass feeding may account for about half the total solidification shrinkage found with these alloys.<sup>50</sup>

Needless to say, the mass-feeding process is able to take place only during the earlier stages of freezing, and ultimately a stage is reached (when the casting is about 60–80% solid) at which further movement of the liquid/solid mass becomes increasingly difficult owing to coherence of the network of growing crystals.<sup>51, 52</sup> Thereafter such feeding as occurs must take place as the result of movement of liquid through the interdendritic spaces. As already stated this, too, becomes difficult.

The incidence of layer porosity (see p. 276) is closely allied with the phenomenon of mass feeding. The precise causes and mechanism of formation of this kind of harmful porosity are not yet fully understood, although it is clear that it results from the occurrence of faults in the mass-feeding process. Probably the layers arise because, in the final stages of mass feeding (i.e. when the pasty mass is beginning to cohere), the settling process is imperfect; settlement of the pasty mass takes place in one region but not in an adjoining region, a fissure thus forming between the two regions. This fissure is only partly filled with residual liquid, so that it contains numerous cavities when the casting is finally solid.

In general, there are two ways of dealing with the problem of shrinkage in these alloys of long freezing range. In the first, employed when the maximum possible soundness is paramount, directional-solidification methods are used, much as was described above for alloys which freeze by skin formation. However, it has been found that directional freezing alone is insufficient to ensure high soundness in these alloys and that steep temperature gradients towards the feeder are also essential. For example, Ruddle,<sup>53</sup> in experiments with plate castings in aluminium–4½% copper alloy, showed that the tensile strength of specimens taken from the plates was proportional to the temperature gradients existing during the later stages of freezing (i.e. during the period of interdendritic feeding), as shown in Fig. 13. Walther, Adams, and Taylor, in later work in which a wide range of temperature gradients were investigated, obtained closely similar results.<sup>54</sup> No doubt the reason for this is that when temperature gradients are steep the interdendritic channels between the feeder and the more remote parts of the casting are more sharply tapered, and liquid can flow along them more readily. (This really amounts to saying that the liquidus and solidus isotherms are closer together.) For this reason, when using the directional-solidification technique with many castings in alloys of long freezing range, it is desirable to ensure that the temperature gradients are steep. For example, heavy chills may be attached to the end of the casting opposite to the feeder, or exothermic compounds or insulating sleeves may be applied to the feeder.<sup>54</sup>

Steep temperature gradients are not set up in a casting the moment freezing begins, but the gradients increase progressively as one end (or ends) of the casting cools, the other end (or central region) being kept hot by the feeder attached there.<sup>53, 55</sup> These gradients increase to a

maximum value and then decline, the cycle being completed quickly in castings of thin section in alloys of low heat capacity and slowly in castings of heavy section in alloys of high heat capacity. Since, for good feeding, it

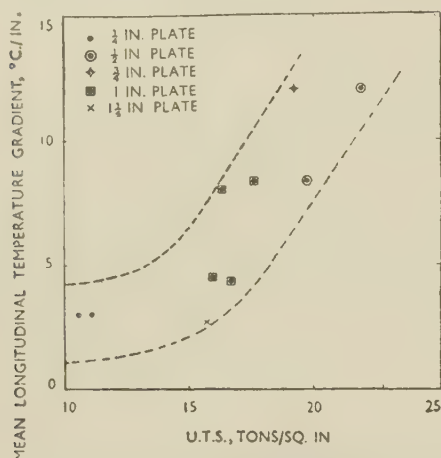


FIG. 13.—The Effect of Temperature Gradient in the Final Stages of Freezing on the Tensile Strength of Plates in Aluminium-4½% Copper Alloy.

is necessary that the temperature gradients prevailing near the end of freezing should be steep, it follows that there is an optimum section thickness for maximum soundness in unchilled sand castings in a given alloy.<sup>53</sup> Thinner sections will freeze before steep gradients are established and thicker ones well after the gradients (which will in any case not be very steep) have passed their maximum. Furthermore, this optimum section thickness will increase with decrease in the heat capacity of the alloy.<sup>46</sup> Thus, whereas the optimum thickness is about ½ in. (or 1 in. dia.) for an aluminium alloy,<sup>53</sup> section thicknesses about double this are the optimum for magnesium alloys.<sup>46</sup>

The matter is even more complicated, for, as has been illustrated by Jackson,<sup>50</sup> in the absence of steep temperature gradients towards the feeder the feeder itself may well make things worse rather than better. Jackson found that in the case of a leaded gun-metal block casting, 4 × 4 × 8 in., as the feeder (attached to the top surface) was increased from a size far too small to yield directional freezing to a size more than sufficient for this purpose, the porosity of the casting fell to a minimum and then increased again (Fig. 14). This increase is attributed to the mass of the larger feeders so slowing the solidification of the casting that the favourable temperature gradients were reduced. Jackson concluded that in the absence of steep temperature gradients high soundness is not attainable in the casting, and feeder size is important only in so far as it provides hydrostatic pressure to prevent local surface sinks. This is illustrated by the lower curve in Fig. 14, which shows that the volume of the casting increased steadily with increase in feeder volume; correspondingly the incidence of surface sinks was reduced and, in due course, eliminated. It seems reasonable to conclude that with these alloys the height of the feeder is its most important dimension.

Small cavities in a casting, provided that they are rounded and not present in severe local concentrations, do not greatly affect its strength (see Section IV. 2, p. 287),

and for many purposes a certain amount of well-distributed porosity of this kind is relatively harmless. An alternative method of dealing with the problem of shrinkage in castings of these alloys is therefore to tolerate a moderate amount of microporosity and to seek to ensure that this is distributed throughout the casting as uniformly as possible. If this approach is adopted, a different feeding technique is used, the gates being introduced into the casting at locations remote from the feeders and preferably into the thinner sections. The feeders themselves are small and are used only to prevent the occurrence of local sinks and to promote a certain amount of mass feeding.

#### (c) The Type, Size, and Effective Range of Feeders

Feeding practice raises certain problems of a more quantitative nature, for example the calculation of the appropriate size of feeder to attach to a casting. Various methods<sup>27</sup> have been suggested for doing this where directional-solidification methods are employed, most of them being based on Chvorinov's rule, the assumption being made that the casting will be sound provided its  $(V/A)$  ration is less than that of the feeder. This rule, although approximate (see p. 276), probably holds well enough for feeder-size calculations provided a sufficient factor of safety is employed. On the basis of this rule, several workers have produced equations for calculating feeder sizes for steel castings.<sup>27, 55, 56</sup> However, although this method may be satisfactory for "chunky" castings, it will not necessarily work well with castings which

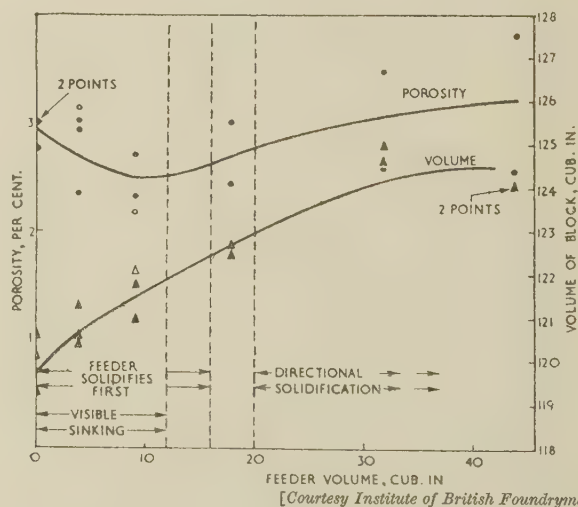


FIG. 14.—Effect of Feeder Size on the Volume and Porosity of a Casting 4 × 4 × 8 in. in 85:5:5:5 Leaded Gun-Metal. (Jackson.<sup>50</sup>)

- ▲ Plaster-sleeved feeder.
- △ Exothermic-sleeved feeder.

have considerable length, for example bars, rods, or long plates. As has been shown by Pellini and his co-workers,<sup>56-58</sup> with steel castings of these shapes, the effect of a feeder will be manifested only for a certain distance down the casting. Pellini and his colleagues have, in fact, carried out a large amount of work on the feeding range of feeders attached to steel castings and have systematized their results in the form of feeding-range equations.



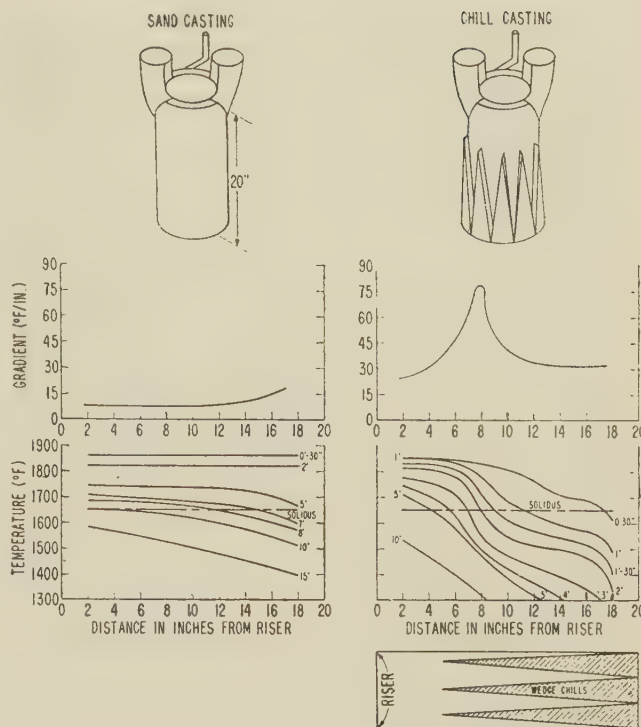
For example, they state that long plates fed by a single feeder at one end are invariably sound for a distance of  $2\frac{1}{2}T$  from the end of the plate remote from the feeder, where  $T$  is the plate thickness; in addition, there is a region  $2T$  long next to the feeder which is also essentially sound. Thus, although a single feeder is capable of ensuring soundness in a plate  $4\frac{1}{2}T$  long, most of the feeding effect ( $2\frac{1}{2}T$ ) is due to chilling from the edges and only  $2T$  to the feeder itself. It seems unlikely that these relations can be applied without modification to non-ferrous alloys which freeze in a near-skin-forming manner, and research to derive similar equations for these materials is most desirable. Pellini<sup>59</sup> mentions that the feeding range (including edge effects) for a high-tensile brass plate is  $5\frac{1}{2}T$ , as compared with  $4\frac{1}{2}T$  for a low-carbon steel plate.

#### (d) The Use of Chills

The effect of chilling has been investigated in some considerable detail, in particular by Pellini and his co-workers, with steel castings.<sup>60, 61</sup> These investigators have shown that the effect of a chill placed at the end of a plate or bar, opposite to the feeder, is to increase the feeding range by 2 in. (plates) or  $T$  in. (bars). Again, similar work on non-ferrous castings is urgently necessary.

One purpose of a chill is to aid directional solidification in skin-forming alloys, as described above. Another is to steepen the temperature gradients present during the freezing of castings in alloys of long freezing range, and Pellini and his colleagues<sup>62</sup> have suggested the use of taper chills for this purpose, as depicted in Fig. 15. The lower sets of curves in Fig. 15 show the temperature distribution at various times after casting, and the upper curves give the temperature gradients present in the final stage of freezing, which are markedly steeper in the chilled casting. They state that by the use of such chills it is possible to make gun-metal castings highly sound even when the metal from which the castings is produced is gassy. Another important application of chilling practice is to minimize the effects of ribs, bosses, &c., attached to a casting, and here again Pellini and his co-workers have conducted much useful work with steel castings<sup>61</sup> which deserves repetition with non-ferrous materials. Pellini's work enables the size of chill required to neutralize a boss or rib to be computed from the dimensions of the casting and of the appendage. The results of this work permit determination of the correct feeding technique for many steel castings in a more or less scientific manner, taking into account the correct size of feeder, the feeding range of the feeders and hot spots, &c., produced by bosses and other appendages.<sup>56, 63</sup> Methods of applying the data obtained by Pellini *et al.* have been described in the literature.<sup>56</sup> Similar experimental work with non-ferrous alloys would be most valuable and should enable the feeding of castings in these alloys to be placed on a firm basis.

It will be appreciated that the above remarks refer principally to alloys which freeze in a skin-forming or near-skin-forming manner. In the case of alloys which freeze in the pasty manner, the size of the feeders used does not appear to be so important, but data on the steepness of the temperature gradients produced by feeders and chills of a given size would be extremely useful. Unfortunately these data are at present meagre.



[Courtesy American Foundrymen's Society.]

FIG. 15.—Effect of Taper Chills on the Temperature Gradients During Freezing of a Hollow Cylinder in Gun-Metal. (Johnson, Bishop, and Pellini.<sup>62</sup>)

#### (e) The Efficiency of Feeders

Because feeders usually depend for their action on solidifying less quickly than the adjacent parts of the casting itself, it is clearly desirable that the shape of the feeder shall be such that the rate at which heat is lost is as small as possible for a given feeder volume. The ideal shape from this standpoint is a sphere—unfortunately often impracticable—and the next best a cylinder (if possible with spherical ends). Rectangular shapes are considerably less efficient, their freezing time being 20% or more shorter than that of a cylinder. The cylinder is therefore usually the best practical compromise between thermal efficiency and mouldability.

Considerable attention has been devoted to methods of improving the efficiency of feeders, and from this point of view it is instructive to consider the way in which heat is lost from a feeder. In general, three mechanisms operate: (i) conduction through the mould walls; (ii) radiation from the (exposed) upper surface of the feeder; and (iii) convection from the upper surface of the feeder.

Adams and Taylor<sup>64</sup> have considered this question in some detail and have shown that the convective loss is small and may generally be neglected. They show, for example, that with a  $4 \times 4$ -in.-dia. feeder with an open top, made in aluminium, the main loss of heat is through the mould walls, only 8% being lost by radiation. On the other hand, with a similar copper feeder the radiation loss is 26% of the total, and in the case of a steel feeder it is 42% of the total loss. Furthermore, the proportion of the heat lost as the result of radiation increases with increase in the size of the feeder. For example, the radiation loss from an  $8 \times 8$ -in.-dia. steel feeder is 55%

of the total as opposed to 42% for a 4 × 4-in.-dia. feeder. There is therefore little to be gained by covering the top of an aluminium feeder, but a useful increase in feeder efficiency will result from covering copper or steel feeders with some insulating material.

Obviously, the freezing time of the feeder can be greatly extended by insulating the side walls from the mould material, and various materials such as plaster are used for this purpose. As Fig. 16 shows, substantial increases in the freezing time result from such insulation. Furthermore, the radiation loss from open insulated feeders is a much larger proportion of the total, and the case for covering the top of the feeder is greatly strengthened. Even higher feeder efficiencies can be produced by means of exothermic sleeves, and in many cases their use enables the volume of metal contained in the feeder to be reduced to as little as 20–30% of the volume of the casting. A considerable improvement in casting yield is the

liquid,<sup>68</sup> but such healing is often incomplete, particularly when it is opposed by atmospheric pressure in open tears.<sup>37</sup>

It follows that the alloys most prone to hot tearing are those which:

(i) have long freezing ranges in which considerable cooling contraction must occur before freezing is completed,<sup>51, 52, 68</sup> and

(ii) contain only small quantities of eutectic, so that nearly all freezing takes place while the temperature is falling and very little at the constant eutectic temperature, at which no cooling contraction need occur in the dendrite network;<sup>68</sup> in sand-cast aluminium alloys, for example, the hot-tearing properties are poor when the volume fraction of eutectic is less than 0.1–0.3, depending on the freezing range.

Hot tearing in hypoeutectic casting alloys is therefore generally least in compositions within the specified range

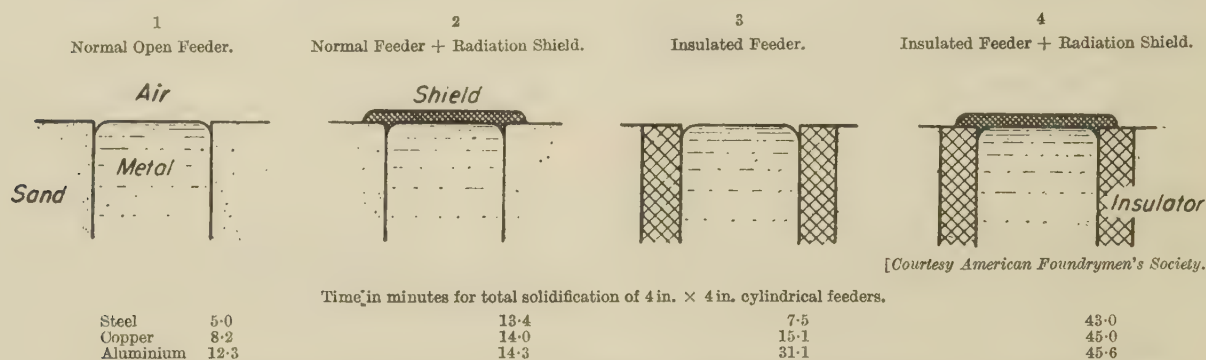


FIG. 16.—Effect of Various Insulating Techniques on the Efficiency of Feeders for Aluminium, Copper, and Steel Castings. (Adams and Taylor.<sup>64</sup>)

result.<sup>65, 66</sup> For example, the casting yield with a particular casting in aluminium bronze as normally cast was 59%; the use of plaster sleeves with exothermic plugs in the top increased the yield to 73%, and adoption of exothermic sleeves and plugs further increased the yield to 80%.<sup>67</sup>

It may be concluded that, except with small castings in long-freezing-range alloys of low melting point, blind feeders of the Taylor–Rominski type or at least feeders whose tops are covered should always be employed to promote maximum efficiency. Production economics will usually permit the use of improved feeding techniques, such as insulating or exothermic sleeves, with larger castings.

#### 4. OTHER DEFECTS FORMED DURING SOLIDIFICATION

##### (a) Hot Tears

Once the dendrites have grown large enough to interlock during solidification, any restraint on their contraction by the mould or other parts of the casting during further cooling may cause the network of dendrites eventually to tear; for while the network is rigid enough to prevent the metal flowing like a liquid when strained, its strength and ductility remain very low as long as liquid films are present between the grains.<sup>51, 68</sup> The tears may be partly healed by the influx of residual

which are nearest to the eutectic; comparative values for the hot-tearing properties of a wide range of aluminium alloys have been published.<sup>69</sup> Traces of low-melting-point constituents due to impurities should obviously be avoided if they are known to wet the grain boundaries; conversely, low-melting-point constituents such as lead in copper, which form globules instead of intergranular films, are relatively harmless. Certain constituents which form intergranular films may be converted to less harmful globules by a suitable addition; sulphur, for example, is particularly deleterious in nickel-base alloys unless magnesium (approx. 0.1%) is added.

The liberation of dissolved gas during solidification reduces hot tearing by assisting the healing process<sup>70</sup> and may prevent the formation of those tears which are due to the collapse of the skin of the casting into underlying shrinkage cavities. A high gas content is therefore useful in castings prone to hot tearing, particularly those cast in rigid mould materials.

Tearing is more pronounced, the more localized the strain.<sup>71, 72</sup> Consequently, the most useful measure in eliminating hot tears is generally to avoid the formation of hot spots between the parts of the casting gripped by the mould (or by the already solid parts of the casting). The use of chills, care in the positioning of gates, and the use of multiple-gating systems are the most effective methods of achieving uniform cooling.

Finally, grain refinement causes a considerable diminu-



tion in hot tearing, as described below, because: (i) the strain due to contraction is distributed over a larger number of grain boundaries,<sup>72</sup> and (ii) the finer dendrites interlock at a later stage of solidification, with the result that the temperature range in which cooling contraction may give rise to hot tears is reduced.<sup>38</sup>

### (b) Segregation

Segregation in sand castings of solid-solution alloys is generally of the inverse type, and although its causes have been discussed in numerous papers,<sup>73-75</sup> its extent is perhaps not often appreciated. Briefly, it results from the fact that parts of the casting in which freezing is most advanced are fed by liquid metal from adjacent regions from which solid-solution dendrites have already deposited, and which is therefore enriched in solute elements. Consequently, the well-fed parts of a casting remote from the feeder have higher than average alloy contents, while the porous regions in the feeder are grossly depleted of alloying elements. In aluminium-10% magnesium alloys, for example, the sound parts of the casting may contain almost 1% more magnesium than the original melt, the feeder being correspondingly depleted;<sup>47</sup> poorly fed castings contain considerably less segregation.

The defect is aggravated by an excessive gas content, which causes residual liquid to be exuded through the surface of the casting as films or blebs, e.g. tin sweat in bronzes.<sup>73-75</sup> Apart from removing high gas contents, however, there is little the foundryman can do to avoid segregation within the casting, though chilling reduces the extent of the segregated regions. Published information suggests<sup>38</sup> that grain-size has little or no influence on segregation in sand castings except in magnesium alloys, where a coarse grain-size is conducive to surface exudations.<sup>76</sup>

### (c) Intermetallic Constituents

Certain of the constituents of most casting alloys form brittle intermetallic compounds, the presence of which tends to reduce the mechanical properties. Compound formation is particularly marked in aluminium casting alloys, but traces at least of a brittle second phase are present between the dendrite arms in other casting alloys.

The most harmful intermetallic compounds are those which form at an early stage of solidification, e.g. by primary deposition, as the crystals of the compound are then large and may segregate in the crucible or in heavy sections of the casting. Precautions are therefore taken to avoid compositions in which intermetallic constituents are precipitated in primary forms, particularly when making secondary casting alloys likely to contain large amounts of impurities. For example, if the sum of the iron content +  $1\frac{1}{2}$  times the manganese content exceeds about 1-1 $\frac{1}{2}$ % in aluminium-copper-silicon alloys, segregation of primary iron-rich and manganese-rich constituents is likely to occur.<sup>77</sup> Similarly, iron contents above about 0.8% in aluminium-silicon eutectic alloys cause the formation of large plates of  $\beta$ -AlFeSi, which seriously embrittle the casting; the addition of manganese to these alloys encourages the formation of less harmful  $\alpha$ -Al(Fe,Mn)Si script.<sup>78, 79</sup>

Much smaller amounts of insoluble intermetallic compounds affect the properties of those alloys in which high tensile properties are normally obtained by dissolving

the brittle interdendritic constituents. For this reason, the iron content is limited to about 0.2% in aluminium-4 $\frac{1}{2}$ % copper alloy, to avoid the formation of large plates of  $N$ -AlCuFe; the silicon content is similarly limited in aluminium-10% magnesium alloy in which large  $Mg_2Si$ -script particles would otherwise be formed.<sup>80</sup> The small quantities of insoluble constituents permitted in these alloys are useful, however, in that they prevent grain growth during solution-treatment.<sup>81</sup>

The mechanical properties can be improved by refining the particle size of intermetallic constituents; the embrittlement caused by such particles, therefore, is probably largely a notch effect and is not simply due to the reduction in the proportion of solid solution in the cross-section of a test-piece, except when continuous intergranular films exist. The most effective method of refining the particle size is to increase the freezing rate, and the tolerable amounts of an intermetallic constituent are therefore greater if the casting is chilled.<sup>82</sup>

Porosity and intermetallic constituents in cast alloys are therefore analogous in that: (i) their notch effects are similar, and (ii) the forms of both can be made less deleterious by control of composition and freezing rate. Other methods are available for controlling the form of porosity, as described elsewhere (p. 287); grain-size, for example, often has a beneficial influence on porosity, though it has little or no effect on the particle size of intermetallic constituents.

Intermetallic constituents lying across grain boundaries tend to obstruct grain-boundary movement at elevated temperatures. Provided that continuous intergranular films can be avoided, therefore, an improvement in elevated-temperature creep properties can sometimes be obtained by the addition of constituent-forming elements. The nickel-bearing constituents in heat-treated Y alloy appear to act in this way.

## IV.—CONTROL OF METAL QUALITY

### 1. THE CONTROL OF GAS CONTENT

#### (a) Porosity Due to Hydrogen Evolution

The release of hydrogen from solution in elemental form is the principal cause of gas unsoundness in all non-ferrous alloys which contain insufficient oxygen to react with the dissolved hydrogen. These include alloys based on magnesium or aluminium, those copper-base alloys which contain more than 10-20% zinc or a trace of aluminium, and nickel-base alloys containing similarly strong deoxidizers.

The solubilities of other elemental gases are too low to form appreciable porosity in the commonly used non-ferrous casting alloys.

Dissolved hydrogen comes into equilibrium with the gas in contact with the melt in accordance with the following equations:



Application of the laws of mass action shows that the concentration,  $S$ , of dissolved gas is proportional to the square root of the hydrogen pressure,  $p_{H_2}$ :

$$S = k\sqrt{p_{H_2}} \quad . \quad . \quad . \quad (11)$$

while the proportionality constant,  $k$ , and thus the hydrogen solubility, increase with temperature. A similar

relationship governs the solubility of hydrogen in the solid metal, but the values of  $k$  (i.e. the solubilities) are considerably lower than for the liquid; it is this fall in solubility during solidification, rather than the much smaller change when the liquid cools from the pouring temperature to the freezing point, that is the primary cause of gas evolution and unsoundness in the casting. Values for the solubility of hydrogen in several pure metals in the solid and liquid states are given in Table V.<sup>83</sup> These

TABLE V.—Solubility of Hydrogen in Some Commonly Used Non-Ferrous Metals.<sup>83</sup>

Metal	Solubility of Hydrogen, c.c./100 g. (at N.T.P.) under 1 atm. H <sub>2</sub> :		
	In Solid Metal at Melting Point	In Liquid Metal at Melting Point	In Liquid Metal at 100° C. above Melting Point
Aluminium	0.034	0.71	1.3–1.4
Copper	1.9	5.2	5.6
Magnesium	Approx. 15	Probably 20–30	Approx. 25–30
Nickel	Approx. 14	Approx. 40	Approx. 42

figures suggest that aluminium and (to a lesser extent) copper alloys, in which the solid solubility of hydrogen is low, should be most prone to unsoundness due to hydrogen evolution; this is in accordance with practical experience. Much larger quantities of hydrogen can be tolerated in a magnesium alloy melt, owing to the higher solid solubility, and hydrogen is rarely absorbed in these amounts because melting is invariably conducted under a flux cover.

Some alloying additions have an appreciable influence on the solubility of hydrogen, as illustrated by the available data listed in Table VI,<sup>83</sup> but it is doubtful whether

TABLE VI.—Effect of Some Common Alloying Elements on Solubility of Hydrogen.<sup>83</sup>

Base Metal	Temperature, °C.	Alloying Addition, wt.-%	Increase in Hydrogen Solubility (% of solubility in pure liquid metal at same temperature)
Aluminium	700	Copper, 5	–30
		Silicon, 6	–30
		„ 12	–40
Copper	1200	Tin, 10	–25
		Nickel, 10	Approx. +50
		Aluminium, 10	„ –50

this influence is great enough materially to extend or shorten the degassing treatment necessary to prevent unsoundness. The effect of alloying additions on the solidification range, on the other hand, has a much more important influence on both the amount and the distribution of unsoundness caused by a given hydrogen content, in the following manner suggested by Ransley.<sup>84</sup>

Hydrogen dissolved in the melt is largely retained in supersaturated solution on freezing, and the quantity of gas in excess of the solid solubility then tends to diffuse from the dendrites of solid into the residual liquid. In a pure metal solidifying by skin formation, the newly deposited solid rapidly becomes isolated from the liquid

metal, and little of the gas may diffuse into the liquid to form porosity in the time available, particularly at the high freezing rates existing in a small casting. If an alloying addition is made which results in an extension of the freezing range, however, the dendrites of solid remain in closer and more prolonged contact with the interdendritic liquid during freezing, and gas may then more readily diffuse into the residual liquid to form bubbles, which are immediately trapped between the dendrite arms. Porosity formation is thus encouraged by alloying elements which prolong the freezing range and increase the proportion of low-melting-point eutectic; however, the curves plotted in Fig. 17, showing the relationship

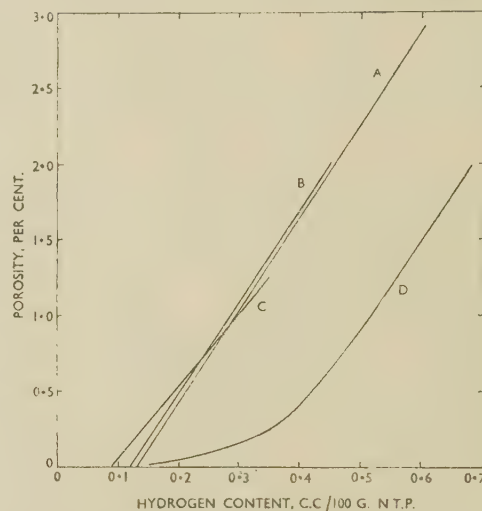


Fig. 17.—Effect of Hydrogen Content of Melt on Porosity of Sand-Cast Bars in Pure Aluminium and Aluminium Alloys.

KEY

- Curve A. 98.8% Al and Al-1.7, 6, or 12% Si. (Deoras and Kondic.<sup>85</sup>)  
 „ B. 99.2% Al. (Ransley and Neufeld.<sup>86</sup>)  
 „ C. Al-4.6% Cu. (Metcalf.<sup>87</sup>)  
 „ D. 99.99% Al. (Ransley and Talbot.<sup>88</sup>)

between hydrogen content and porosity for small sand-cast test-pieces of various aluminium alloys and high-purity aluminium,<sup>85–88</sup> indicate that the maximum porosity for a given gas content is probably formed when quite low percentages of alloying elements are present, at the freezing rates obtaining in such castings. (This is not the case at the higher freezing rates in chill castings.) The curves in Fig. 17 also show that a hydrogen content well above the solid solubility is generally required before porosity can be detected in small sand castings of aluminium alloys, a certain amount of hydrogen being retained in supersaturated solution when the last traces of liquid freeze. Quantitative information of this type for hydrogen in copper-base alloys is not yet available.

The pressure at which gas bubbles form in aluminium alloys can be estimated from the relationship between porosity and gas content to be just over an atmosphere,<sup>86, 88</sup> i.e. bubbles form when the internal gas pressure exceeds the pressure over the melt. There is little evidence that bubble formation is normally assisted by nucleation on the surface of stray particles in the melt, the presence of the solid/liquid interface during solidification probably being sufficient to promote bubble formation. It has been observed, however, that melts of aluminium or aluminium-copper which have been de-



gassed with carbon tetrachloride or hexachlorethane contain carbon inclusions under certain conditions; such melts form bubbles very readily in the reduced-pressure test and the response, moreover, is greatly influenced by stirring the melt from which the test sample is removed, or by allowing it to settle.

### (b) Unsoundness Due to Compound Gases

A number of compound gases may be evolved during the solidification of alloys capable of dissolving oxygen.<sup>89-91</sup>

In copper, for example, hydrogen or sulphur in solution may react with oxygen to form steam or sulphur dioxide, respectively:



$$K = \frac{[\text{O, wt.-%, in Cu}] (\text{H}_2 \text{ pressure})}{(\text{H}_2\text{O pressure})} \quad (13)^*$$

$$= 2.9 \times 10^{-7} \text{ at } 1100^\circ \text{C.}$$

$$6.0 \times 10^{-7} \text{ at } 1200^\circ \text{C.}$$

$$11.5 \times 10^{-7} \text{ at } 1300^\circ \text{C.}^{92}$$



$$K = \frac{[\text{O, wt.-%, in Cu}]^2 [\text{S, wt.-%, in Cu}]}{(\text{SO}_2 \text{ pressure in mm. Hg})} \quad (15)$$

$$= 1.1 \times 10^{-5} \text{ at } 1100^\circ \text{C.}$$

$$2.4 \times 10^{-5} \text{ at } 1200^\circ \text{C.}$$

$$4.4 \times 10^{-5} \text{ at } 1300^\circ \text{C.}^{93}$$

Carbon (in addition to hydrogen and sulphur) is soluble in alloys containing considerable proportions of nickel (more than 10%), and may react with oxygen to form carbon monoxide:



In each case the solubility of the compound gas falls with the temperature of the melt, but, nevertheless, the metal rarely in practice becomes saturated before solidification begins unless the melt is deliberately oxidized in the furnace, as described below. During freezing, however, both constituents of the gas tend to segregate in the residual liquid, and their concentrations may eventually rise sufficiently to allow the pressure of the gas in equilibrium with them to exceed 1 atm., with the consequent formation of bubbles between the dendrite arms. The stability of steam, in particular, is such that its partial pressure is higher than that of hydrogen in the presence of the traces of oxygen usually found in alloys free from powerful deoxidants; steam evolution causing unsoundness may occur in these alloys, therefore, when the hydrogen content would otherwise be quite insufficient to produce bubbles of hydrogen, and consequently more vigorous degassing treatments are required.<sup>90, 91</sup>

As would be expected, the formation of porosity due to compound gases is influenced in the same way as hydrogen unsoundness by freezing rate and alloy constitution, but quantitative information on these aspects is exceedingly scanty.

### (c) Sources of Dissolved Gas

Oxygen pick-up during melting can be greatly reduced by covering the melt with a thick bed of charcoal, but the

traces of oxygen remaining or dissolved on pouring (at least 0.001% in copper) are sufficient to cause evolution of compound gases unless removed by the methods described in Section IV. 1 (e). Sulphur and carbon may be picked up either from the charge (and the crucible) or from the burnt fuel, particularly under reducing conditions, and the contents of these elements can be limited by controlling the furnace atmosphere and the composition of the charge and the fuel, though this is not always practicable.

Hydrogen is formed during melting by reaction with steam in the furnace gases, but moisture on the tools and ladles, in the flux, or in corrosion products on ingots added to the bath, is also a common source of hydrogen. If sources of moisture other than the furnace gases are excluded, the hydrogen pick-up can be controlled adequately for many purposes simply by limiting the temperature of the melt and preventing direct contact between the flame and the surface of the metal, as the reaction with moisture and the consequent hydrogen pick-up increase sharply with temperature; for example, the hydrogen content of pure aluminium in an oil-fired furnace may increase from 0.2 c.c./100 g. at 750°C. to 0.6 c.c./100 g. at 900°C., according to measurements reported by Ransley and Talbot.<sup>88</sup> The hydrogen pick-up is also accentuated by the presence of highly reactive alloying elements in the melt, e.g. magnesium in aluminium and phosphorus in copper, but a flux cover may help considerably in retarding the reaction by acting as a barrier between the metal and the furnace gases.

Certain of the alloys containing reactive elements, even when cast with a low gas content, may absorb considerable quantities of hydrogen by reaction with steam in the sand mould, i.e. by "mould reaction".<sup>95, 96</sup> The reaction is generally stifled by the oxidation product when this consists of a coherent oxide film (e.g. that formed on aluminium bronze and most aluminium alloys); however, some additions not only react readily with steam because of their high affinity for oxygen, but also result in the formation of non-protective oxidation products such as a liquid which gathers up into globules (e.g. phosphorus in a tin bronze) or a powdery oxide (magnesium in aluminium), and mould reaction then continues unabated until solidification is nearly complete.<sup>96</sup> The extent of mould reaction depends on the concentration of the reactive element and may become catastrophic at high concentrations, e.g. in magnesium-base alloys. Similarly, the addition of a reactive element forming a non-protective oxidation product may allow other reactive elements to contribute to mould reaction; for this reason, phosphorus additions as small as 0.03% cause appreciable mould reaction in copper alloys containing zinc, whereas 0.2 or 0.3% phosphorus is necessary in tin bronzes free from zinc and similarly reactive elements.

Mould reaction in aluminium-10% magnesium alloys continues during solidification; the rate of reaction is reduced by the fall in temperature through the freezing range but enhanced by the rise in magnesium content of the residual liquid, with the result that the overall rate of reaction reaches a maximum near the solidus.<sup>97</sup> The hydrogen formed at such a late stage of solidification cannot diffuse far into the casting, and therefore results in a concentration of hydrogen unsoundness near the

\* The pressure units are immaterial provided they are the same for both gases. The hydrogen pressure is proportional to the square of the dissolved hydrogen content.

surface, together with a layer of powdery oxide if the reaction is not inhibited. In tin bronzes and gun-metals, on the other hand, no increase in oxide formation on the surface can be detected when phosphorus is present and the hydrogen arising from mould reaction diffuses towards the heat centres of the casting, unsoundness being created throughout the section rather than near the surface.<sup>95</sup> In either case, the reaction proceeds further at slower freezing rates, and is therefore particularly marked in large castings; <sup>98</sup> conversely, mould-reaction effects in all alloys can be reduced by chilling.

Fortunately, chemical methods of inhibiting the reaction are available for most of the alloys concerned. Magnesium-base alloys can be cast safely into sand containing about 5% sulphur, the reaction then being stifled by sulphide films; boric acid is also used as an inhibitor. Similarly, mould reaction in aluminium-magnesium alloys can be controlled by adding boric oxide or ammonium bifluoride to the sand (sulphur is not effective); considerably more effective inhibition is obtained by adding 0.004% beryllium to the metal, which evidently makes the oxide film less permeable, but chilling is also necessary in castings of more than 3-5-in. section thickness, as inhibition is not otherwise complete even when additions are made both to the metal and to the sand.<sup>98</sup> Elements forming tenacious oxide films (e.g. silicon) prevent mould reaction in bronzes and gun-metals, too, but the good casting properties of the alloys are lost if such elements are added; <sup>95</sup> a more acceptable method is to spray the mould with aluminium or aluminium-magnesium paints, which protect the casting partly by sacrificial oxidation and partly by forming alumina films.<sup>99</sup>

#### (d) Tolerable Limits of Gas Content

The limit to which the gas content should be reduced depends largely on the composition of the alloy and the degree of soundness necessary in the casting.

In most high-strength aluminium alloys, the highest tensile properties are obtained only from well-fed castings of degassed metal, but the alloys differ in the amount of gas they can tolerate, as shown by comparison of curves (A) and (B) in Fig. 18,<sup>47</sup> and the degassing treatment should be selected accordingly; the high sensitivity to gas of the aluminium-magnesium alloy is due to the formation of layer porosity discussed above (p. 276). The aluminium alloys of lower strength, such as the aluminium-copper-silicon and aluminium-silicon alloys, can tolerate considerably more gas porosity, up to at least 1%, as they already contain large proportions of intermetallic constituents which weaken the alloy; moreover, the gas voids tend to be more rounded and less deleterious than in the high-strength alloys, owing to the greater volume of eutectic liquid from which the cavities are formed. Well-fed castings in gun-metals and bronzes may contain even more gas porosity, up to 1-2% as shown in Fig. 19, without the tensile properties being affected significantly <sup>95</sup> (provided that the grain-size of the alloy is not refined, as layer porosity would then cause a sharp fall in strength and ductility); <sup>37</sup> quantitative information on other copper alloys is lacking, but their permissible porosities are probably at least as great as in the gun-metals.

Larger amounts of dissolved gas can be tolerated and may even be advantageous in poorly fed castings. Not

only are hot tears and surface draws or sinks less marked when gas is liberated, but also porosity tends to be more uniformly distributed within the casting.<sup>95</sup> In those alloys in which lack of feeding results in the formation of layer porosity, the effects of shrinkage on tensile properties are much more deleterious than those of gas (compare curves (B) and (C) in Fig. 18) and a moderate gas

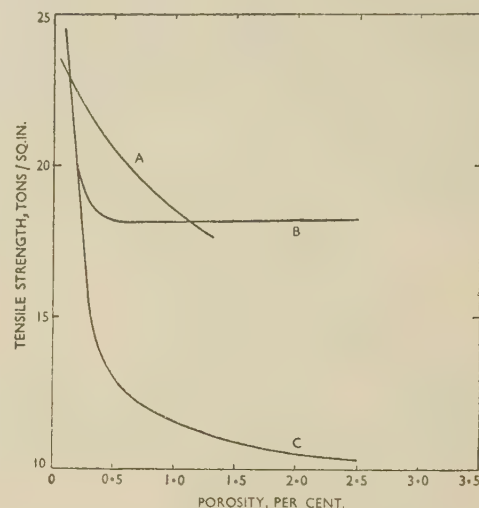


FIG. 18.—Influence of Shrinkage and Gas Porosity on Tensile Strength of Aluminium-11% Magnesium and Aluminium-4½% Copper Alloys, Grain Refined and Sand Cast. The test casting was a 1-in.-dia. bar and feeders of various sizes were used.

#### KEY

- Curve A. Gas or shrinkage porosity in Al-4.5% Cu.  
 " B. Gas porosity in well-fed Al-11% Mg. (Gassy metal.)  
 " C. Shrinkage porosity in Al-11% Mg. (Degassed metal.)

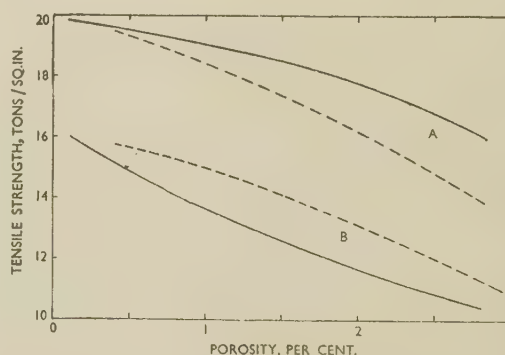


FIG. 19.—Influence of Gas Porosity on the Tensile Strength of 1-in.-dia. Sand-Cast Bars of (A) Lead-Free 88:10:2 and 88:8:4 and (B) Leaded 85:5:5:5 Gun-Metals, Both Deoxidized with Phosphorus.

- Porosity due to gas dissolved in melt.  
 — Porosity caused by mould reaction.

content—say, 0.4 c.c. H<sub>2</sub>/100 g. in aluminium alloys—markedly raises the tensile properties of poorly fed sections, the cavities becoming more rounded than in the absence of gas.<sup>47</sup>

When pressure-tightness is the property of greatest concern, the distribution of porosity may be as important as the amount. Most aluminium alloys possess little or no sound skin of columnar grains, and interdendritic



porosity in excess of  $\frac{1}{2}$ –1%, whether due to gas or lack of feeding, causes leaking; a low gas content and adequate feeding are therefore necessary for pressure-tightness in these alloys. Castings in gun-metals, on the other hand, particularly the leaded alloys, can be made pressure-tight with up to 2 or 3% shrinkage porosity if the macrostructure is largely columnar, as porosity is then concentrated near the centre-line; if the macrostructure is of this type, a further improvement in pressure-tightness can be obtained by introducing a small amount of gas into the metal to restrict feeding, as excessive concentrations of porosity at the heat centres are thus partly dispersed along the centre-line in other sections of the casting.<sup>95</sup> The concentration of gas must be carefully controlled, however, as an excess is harmful, and the most effective method is to degas the metal and add sufficient phosphorus (say, 0.06–0.08%) to cause a moderate degree of

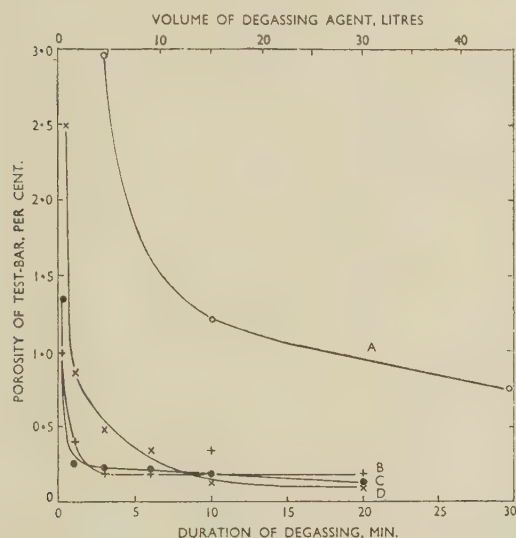


FIG. 20.—The Effect of Degassing Treatments on the Soundness of 1-in.-dia. Sand-Cast Bars of Aluminium-4½% Copper Alloy. 40-lb. melts purged at  $1\frac{1}{2}$  l./min. at 720°C.

#### KEY

- Curve A. Melt allowed to stand in air.  
 " B. Melt purged with nitrogen.  
 " C. " " " chlorine.  
 " D. " " " nitrogen + carbon tetrachloride.

mould reaction. Gas picked up in this way is more effective than gas dissolved in the metal before pouring in redistributing shrinkage porosity. For example, Baker and his colleagues<sup>95</sup> were able to reduce the percentage of small gun-metal test-castings which leaked from 80% to less than 5% in this way; however, the improvement is less marked in castings of  $\frac{1}{2}$ –1 in. section thickness and degassed metal is probably best for thicker sections.<sup>100</sup>

#### (e) The Removal of Dissolved Gas

Much of the hydrogen dissolved in copper or aluminium alloys diffuses through the surface if the melt is allowed to stand in air, as shown in Fig. 20.<sup>101</sup> The process can be made faster for foundry use simply by stirring the metal with a paddle, a flux cover preventing the formation of dross on alloys containing aluminium.<sup>102</sup>

Hydrogen (and other gases) may be removed more

rapidly by purging the melt with an inert gas which is insoluble in the metal.<sup>103</sup> The dissolved gas diffuses into the bubbles of inert gas rising to the surface, the rate of removal becoming slower as the partial pressure falls. The curves in Fig. 20 illustrate the variation in rate of gas removal from an aluminium alloy by several purging gases, and similar results are obtained with copper alloys; it can be shown that the theoretical rate of gas removal would be several times greater than that shown in Fig. 20 if the hydrogen in each bubble reached equilibrium with the partial pressure of gas in the melt, and little would probably be gained, therefore, by using higher rates of flow of the purging gas. Even so, very short degassing treatments of 5 min. or less suffice to remove most of the hydrogen, though more prolonged treatment up to 15 or 20 min. may be necessary to achieve lower gas contents; the lower limit for aluminium alloys degassed under foundry conditions is about 0.1 c.c.  $H_2$ /100 g. at N.T.P.

The internal pressure of dissolved hydrogen falls sharply as the temperature is raised and the rate of hydrogen pick-up from moisture in the atmosphere is simultaneously increased. Consequently, the rate of degassing by purging is low if the metal is too hot, temperatures below 720°C. being preferable for aluminium alloys.

Nitrogen (under a flux cover), chlorine, carbon tetrachloride, and hexachlorethane may be used for purging aluminium alloys.<sup>103</sup> Chlorine-containing materials exert a useful fluxing action, as they form aluminium or magnesium chloride, which removes oxide films as it rises through the bath; magnesium is also removed from the alloy, however. Nitrogen creates no fumes, is cheap but less effective in removing oxide films, and tends to create dross on the surface of the melt if the flux cover is not maintained. Solid carbonaceous materials are often most convenient, but may leave carbon-bearing inclusions under certain conditions. For purging copper alloy melts, nitrogen and air are suitable; materials such as marble or manganese dioxide + carbon, which evolve carbonaceous gases when heated, are also useful scavengers when held at the bottom of the crucible, and a number of proprietary materials with a similar action are available.<sup>91</sup>

Presolidification, followed by rapid remelting, is sometimes utilized to eliminate gas, but the double melting treatment appears to be unnecessary and wasteful.<sup>103</sup>

Gas-forming elements can be removed from melts capable of dissolving oxygen by oxidizing the metal before casting, either: (i) by adding an oxide (e.g. nickel oxide to nickel-base alloys) or an oxide-rich flux<sup>91, 104</sup> (e.g. cupric oxide-boric acid-sodium chloride-sodium fluoride to copper-base alloys),<sup>104</sup> or (ii) by melting under an oxidizing flame.<sup>95</sup> The oxygen concentration is thus raised to the point at which the equilibrium pressure of the compound gas exceeds 1 atm., according to the equilibria described in Section IV. 1 (b), and the gas is then "boiled" from the melt until excess oxygen remains in equilibrium with only a trace of the other constituent of the gas. This oxidation method of degassing is more effective, the higher the oxygen content of the melt, and considerable proportions of elements such as zinc and phosphorus in copper, which limit the oxygen concentration by precipitating oxides, interfere with the process.<sup>95</sup>

If a melt degassed by purging or oxidation were then

allowed to solidify, oxygen remaining in the metal would segregate in the interdendritic liquid during solidification, and cause porosity by reaction with residual traces of hydrogen, carbon, or sulphur. To avoid this a powerful deoxidant is added to the melt; some oxygen may be immediately precipitated as oxide, but the primary function of the deoxidant is to segregate with the residual oxygen during solidification and, by continually precipitating more oxide,<sup>94</sup> to prevent its concentration from rising and thus its reacting with hydrogen, carbon, or sulphur to form compound gases. This treatment may indeed be so effective that prior purging or oxidation of the melt may be unnecessary for many castings, though a purging treatment followed by deoxidation is generally needed if the highest soundness is desired.<sup>95</sup>

Clearly, the deoxidant must have a greater affinity than the gas-forming element for oxygen if the release of gas is to be prevented. Manganese and magnesium are therefore used as deoxidants in nickel-rich alloys, while

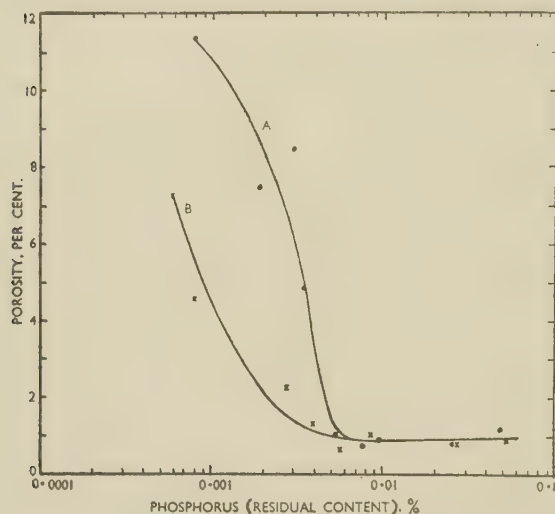


FIG. 21.—The Effect of Residual Phosphorus Content on the Porosity of 6½-in.-dia. Chill-Cast Ingots in Copper-1% Cadmium Alloy, Cast from (A) Gassy and (B) Purged Melts at 1200° C.

phosphorus is preferable for pure copper, gun-metals, and bronzes, because the liquid deoxidation product separates readily from the melt.<sup>94</sup> Pure copper is also sometimes deoxidized with lithium or calcium boride, but these deoxidants do not appear to have any special advantages. After the addition has been made, traces of oxygen and deoxidant remain in solution, usually in equilibrium with the deoxidation product at the pouring temperature. If the residual content of the deoxidant is less than the equivalent of the residual oxygen concentration (the equivalent being calculated from their relative proportions in the deoxidation product), the supply of deoxidant would become depleted by precipitation of oxide at a certain stage of solidification, and it would then be possible for the oxygen concentration to rise.<sup>94</sup> Consequently, there is a critical residual concentration of deoxidant adequate to prevent porosity, which can be determined from: (i) the composition of the deoxidation product, and (ii) the equilibrium between oxygen and the deoxidant at the pouring temperature. For phosphorus in phosphorus-deoxidized copper, copper-cadmium, and

copper-tin alloys, this critical residual content is about 0.005%; the value depends to a small degree on the hydrogen content of the melt, as illustrated in Fig. 21,<sup>105</sup> because a little excess oxygen can be tolerated if the hydrogen content is low. The actual addition to the melt must be greater than the residual phosphorus content required, if the oxygen picked up on melting is sufficient to cause separation of some phosphorus from the melt as slag before the metal is cast; generally an addition of 0.02–0.03% phosphorus is adequate for deoxidation of bronzes and gun-metals.

#### (f) Assessment of Gas Content

A crude test for dissolved gas is to observe the “set” of an open-cast cake, solidified under standard conditions;<sup>106</sup> in aluminium alloys, hydrogen contents down to about 0.6–0.8 c.c./100 g. can be thus detected, while high gas contents are easily confirmed, as they cause the formation of blebs. This test is insufficiently sensitive for most purposes. Attempts have been made to increase the sensitivity of similar tests for gun-metals and bronzes by examining the fracture of a standard cast plate, chilled from one end;<sup>107, 108</sup> although the depth of sound metal and the appearance of the remainder of the fracture are influenced by the gas content, the variable macrostructure, too, has a large effect, and French has concluded that the test (as used so far) is not reliable enough for foundry purposes.<sup>108</sup>

Solidification under reduced pressure (2 cm. Hg.) is a more sensitive test for gas in magnesium-base, aluminium-base, and copper-aluminium alloys;<sup>43, 106</sup> observation of the “set” and bubble formation enables hydrogen contents down to 0.2–0.25 c.c./100 g. to be detected in aluminium alloys. Density measurements increase the sensitivity still further, but the test then becomes too time-consuming for foundry control. A similar objection can be made to the assessment of gas contents by density determinations on sand-cast bars or other test-pieces cast at atmospheric pressure, though such tests may be used with any casting alloy, can be made as sensitive as necessary, and are particularly useful for research purposes; the range of gas contents revealed by such tests is indicated by the results in Fig. 17 (p. 282).

The Ransley gas-tester, which, when calibrated, provides a rapid measure of the hydrogen content of the melt,<sup>109</sup> would prove a most useful piece of apparatus if a model sufficiently robust for foundry conditions were developed. Though devised originally for aluminium alloys, the method should be applicable to copper alloys if suitable materials can be found for the probe unit which is dipped into the melt.

The assessment of gas content by determination of the mechanical properties of a test-bar is discussed in Section IV. 2.

## 2. CONTROL OF GRAIN-SIZE

### (a) Effect of Grain-Size on Mechanical Properties

The mechanical properties of cast metals are often greatly dependent upon the grain-size of the casting, and there may be two reasons for this. In the first place, with some metals at least there is an effect of grain-size *per se*. For example, Pell-Walpole<sup>110</sup> has shown that refining the grain-size of cast tin more than doubles the



strength and a significant increase in strength was also produced by refining the grain-size of cast tin-1% antimony alloy; similar effects have been observed in magnesium alloys.<sup>38</sup> These materials have tetragonal or c.p. hexagonal structures, and are therefore more sensitive to grain-size than metals of cubic structure, such as aluminium. Smaller effects have been found in cast (and wrought) brasses, but the influence of grain-size *per se* is negligible in the other commonly cast alloys of cubic structure.<sup>111</sup>

More important is the effect which grain-size exerts on mechanical properties via its influence on the shape and magnitude of the shrinkage voids inevitably present to some extent in castings in long-freezing-range alloys. Cibula and Rudd<sup>112</sup> have shown that these voids tend

tensile properties is much less marked, since the inter-metallic constituents themselves have a considerable embrittling effect, as discussed above (p. 281).

In addition to its effect on mechanical properties, the grain-size of the casting, as already stated, has an important effect on certain of the casting characteristics, in particular on hot tearing and the extent to which mass feeding occurs. For example, refinement of the grain-size of aluminium-4.5% copper alloy test-bars from 1.5 to 0.2 mm. decreases the amount of shrinkage porosity from 1.5 to 0.2%,<sup>38</sup> this small amount of porosity being widely dispersed.

Unfortunately, with some materials the benefits which accrue from grain refinement are to some extent offset by the fact that the formation of layer porosity is

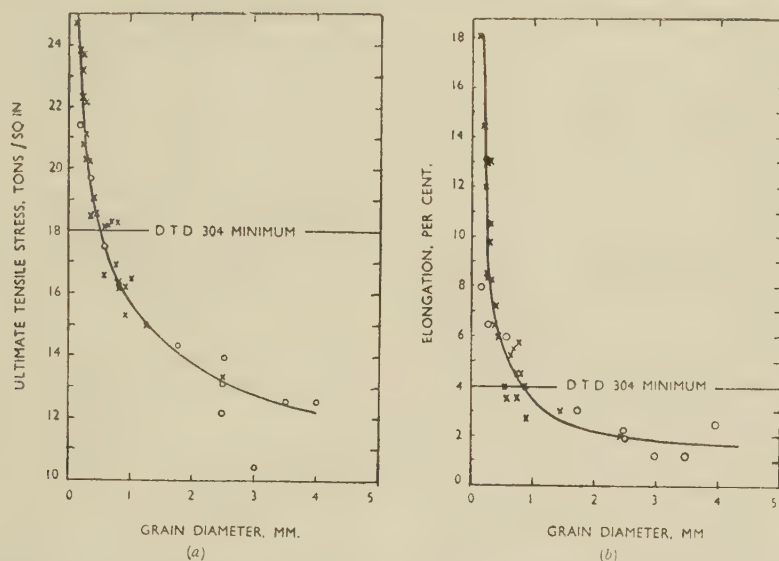


FIG. 22.—Effect of Grain-Size on (a) Tensile Strength and (b) Elongation of Sand-Cast Test-Bars in Aluminium-4½% Copper Alloy After Full Heat-Treatment.

○ denotes melt superheated before casting.

× denotes melt not heated above casting temperature.

to be few in number but relatively large in coarse-grained alloys, being often elongated along the grain boundaries; such cavities naturally have an extremely high stress-raising effect, and hence a most damaging effect on the strength and ductility of solid-solution alloys not already weakened by the presence of intermetallic constituents. On the other hand, in fine-grained material the shrinkage cavities, although much more numerous, are smaller (for a given total porosity in the casting) and are generally equiaxial; such cavities do not greatly affect properties, probably doing little more than reduce them in proportion to the cross-sectional area of the voids. An increase in strength of 75% and in elongation of about 500% may be produced in the high-strength aluminium-4½% copper alloy by reducing the average grain dia. from 4 to 0.2 mm. (Fig. 22).

Effects of this kind vary to a considerable extent with the type of alloy. They are most marked in alloys consisting essentially of hardened solid solutions in which few intermetallic constituents are present. On the other hand, in alloys containing large amounts of intermetallic constituents (many of the lower-strength aluminium alloys are examples), the effect of grain refinement on

greatly accentuated. For example, Cibula<sup>37</sup> found that although grain refinement reduced the porosity of all types of castings in gun-metals and leaded gun-metals, it also resulted in layer porosity, particularly in poorly fed sections; besides generally reducing the strength and ductility of these castings, the layer porosity caused marked deterioration in pressure-tightness. Fortunately when sand cast without grain refiners, these alloys normally possess a columnar macrostructure in which much of the porosity appears at the centre-line and has little effect on pressure-tightness, the skin of the casting being nearly sound. Light alloys, on the other hand, normally possess coarse equiaxial structures in the absence of grain-refining treatments, and grain refinement in these alloys is generally essential for pressure-tightness.

#### (b) Grain-Refining Treatments

Grain-refining treatments are now available for the majority of the commonly used non-ferrous casting alloys. Aluminium alloys may be refined by the addition of 0.05% or more of titanium, but this treatment may not be effective, since the nuclei formed in the melt

(titanium carbide) are readily removed or dissolved if the metal is heated to temperatures much in excess of 700° C.<sup>30, 112</sup> and may not re-precipitate on cooling to the casting temperature. The grain-size of alloys treated with 0.03% titanium and 0.01% boron is much less affected by superheating, the nuclei of titanium boride formed being more persistent than carbide nuclei.<sup>35</sup> Treatment with titanium and boron has, however, a disadvantage in that the titanium boride crystals tend to settle if the melt is left tranquil for long periods, but such segregation can be avoided by making the refining addition just before casting. Both titanium and boron may be added to the melt either in the form of separate master alloys containing 1-5% titanium and 1% boron or by treating the melt with halide fluxes containing these elements, e.g. with titanofluorides or fluoborates. Proprietary materials are now available incorporating compounds of this kind.

Grain-refining treatments carried out on magnesium alloys are of two kinds: (i) treatments in which the metal is stirred with carbon,<sup>113</sup> and (ii) addition of zirconium.<sup>114</sup> It is believed that treatment (i) gives rise to the formation of aluminium carbide particles in the melt which serve as nuclei. This treatment may be effected simply by superheating the metal to a high temperature, e.g. 900° C., in contact with a carbon-containing material, or by introducing carbon from some suitable carbonaceous material such as hexachlorethane. In treatment (ii), zirconium is introduced into the melt from suitable zirconium halide fluxes. It is usually necessary to add about 0.6-0.7% zirconium, and this treatment, which yields an exceptionally fine grain-size (0.05 mm.), has given rise to a new class of magnesium alloys having exceptional properties. Zirconium additions are not effective in alloys containing aluminium, manganese, silicon, and certain other elements, because these elements form highly stable compounds with zirconium, thus withdrawing the metal from the melt.

Bronzes and gun-metals may be refined by addition of 0.05% zirconium,<sup>36</sup> which is normally added as copper-zirconium master alloy. Gun-metals can also be refined by the addition of iron in relatively large quantities (about 1%), but this treatment is not recommended, since it is liable to give rise to rust spots and to hard particles which cause difficulty during machining. Aluminium bronzes and high-tensile brasses normally contain substantial amounts of iron which act as grain refiners, so that these materials are usually fine-grained. Iron-free aluminium bronzes and  $\beta$  brasses may be refined by addition of zirconium (0.03%) and boron (0.02%)<sup>36</sup> or by boron alone<sup>115</sup> in primary  $\beta$ -phase alloys.

As mentioned on p. 287, a columnar structure is frequently desirable in gun-metal castings, especially those subjected to pressure. This kind of structure can be produced by ensuring that the temperature at which the casting is poured exceeds a critical value that depends upon the alloy and the shape of the casting. When castings are poured at a high temperature, turbulence in the liquid metal dies out before freezing begins; in these conditions a coarse columnar structure forms. On the other hand, if the pouring temperature is low, solidification begins almost at once and turbulence in the liquid detaches crystallites from the mould wall as they are formed and transports them into the interior of the cast-

ing, where they continue to grow, an equiaxial structure resulting.

### (c) *Prevention of Grain Coarsening*

Mention has already been made of the grain coarsening which occurs in aluminium alloys containing grain refiners, if the melt is heated to temperatures in excess of 700° C. Removal of nuclei may also take place as the result of: (i) degassing treatments,<sup>30</sup> and (ii) gravity segregation before pouring.<sup>35, 112</sup> For this reason degassing treatments should not be carried out for longer times than necessary, and the melt must be well stirred shortly before pouring.

Local grain coarsening may also arise from settling under gravity (according to Stokes's law) of the crystallites formed in the interior of the casting.<sup>32, 35</sup> As the result of this continuous settling action (which may be upward or downward, according to the density of the crystallites relative to that of the melt) a region at the top (or bottom) of the casting becomes denuded of nuclei upon which freezing can take place. This region therefore eventually freezes by columnar growth from the mould walls. An example of this phenomenon is given in Fig. 23 (Plate XLVII). The only palliative for this condition is to pour the casting at the lowest possible temperature, but this will not always be fully effective in preventing the formation of a region of coarse grain-size.

## 3. ELIMINATION OF INCLUSIONS

### (a) *Sources of Non-Metallic Inclusions Formed During Melting*

Inclusions formed during the casting of metal have already been referred to in Section II. The present Subsection is largely concerned with inclusions which are present in the metal before it is poured. It is true that such inclusions should largely be filtered out in a properly designed gating system, but in practice even the best gating systems cannot always be relied upon completely to prevent these inclusions from reaching the casting, and it is therefore pertinent to consider the way in which the inclusions are formed in the melt and how they may best be prevented. The most important class of inclusions consists of oxides and nitrides of the metals being melted, these oxides being formed through reaction of the melt surface with air, or being present in the raw materials. Such inclusions may be of three distinct kinds:

(i) Powdery dross, which is on the whole relatively harmless, since it rarely penetrates into the casting, being readily trapped in the gating system.

(ii) Oxide skins. This type of inclusion consists of relatively strong films of oxide. These are particularly obnoxious because the skins break up into fragments which pass in the metal stream into the casting.

(iii) Liquid slags. Inclusions of this type may result when the oxidation product of the alloy is liquid at the melting temperature. This type of inclusion is also dangerous, though to a lesser extent than (ii); although the slag can pass easily into the casting, the inclusions formed are usually more or less spherical in shape and therefore less damaging.

In addition, inclusions may result from the use of fluxes in melting, especially the highly fluid type which cannot be readily removed from the melt surface, and



from addition of solid non-metallic materials to the melt, such as charcoal.

Alloy constituents particularly liable to give rise to the oxide-skin type of inclusion are aluminium, beryllium, and silicon, and alloys containing even small quantities of these elements must therefore be handled very carefully in the foundry. Most of the other commonly used alloying constituents give rise to powdery drosses. Certain additions frequently made to copper and nickel alloys, such as phosphorus and manganese, result in liquid deoxidation products. The cuprous phosphate slag formed on phosphorus-deoxidized copper is an example.

Flux and oxide inclusions can easily be introduced into the casting during the direct filling of feeder heads from the crucible; lack of care during this operation cannot be too strongly condemned in alloys which form oxide skins. Inclusions may also be due to mould dressings, particularly in large castings. Many mould dressings of the flaming carbonaceous type burn during casting of the metal and release soot, which is liable to be trapped in the casting.

### (b) Effects of Inclusions

Inclusions which are liquid during pouring and the powdery type of inclusion do not in general have a very damaging effect on the mechanical properties of the casting. Theory suggests that such inclusions might be expected to reduce the mechanical properties in proportion to their cross-sectional area. Oxide-skin inclusions, however, are much more damaging, since they often stretch a considerable way across the section of the casting and, furthermore, tend to impede feeding, thus causing localized regions of severe porosity. Sachs, Dana, and Ebert<sup>116</sup> suggest that the effect of inclusions may be represented by a factor  $R$  defined by:

$$R = \frac{\text{Fractional reduction in tensile strength}}{\text{Volume of inclusions/Volume of casting}}$$

and state that in aluminium alloys  $R$  is about 4 for surface inclusions and 2 for inclusions in the interior of the test-bar, but there is no doubt that oxide-skin inclusions may often be much more damaging than this. Inclusions of the skin type have a particularly disastrous effect upon pressure-tightness, especially of gun-metal castings.<sup>117</sup>

Because inclusions in a casting tend to float to the upper surface during freezing, the finish of this part is often poor when large numbers of inclusions pass into the mould cavity.

Apart from these deleterious effects, the conditions which favour the production of inclusions are also undesirable because they generally result in substantial melting losses, since the inclusions, particularly those of the skin type, tend to trap large amounts of liquid metal when attempts are made to skim the melt. Such effects are particularly prevalent in, for example, aluminium bronzes, where melting losses of up to 10% may occur if proper care is not taken to prevent excessive oxidation.

### (c) Prevention of Inclusions

If inclusions are to be totally eliminated, the melt must be skimmed extremely carefully before pouring, and the pouring stream should be kept as short as possible to minimize breakage of the oxide tube. In addition, a

properly designed gating system which will trap any fragments of oxide skin, &c., which may pass down the sprue, is a necessity. A point of particular importance in connection with skimming is that oxide, nitride, flux, &c., may adhere to the side of the pot during skimming but subsequently pass into the metal stream during pouring.<sup>118</sup> A suggested method of pouring magnesium alloys is indicated in Fig. 24.<sup>118</sup>

The possibility that inclusions of oxide, nitride, &c., may become dispersed in the metal has frequently been discussed in the literature. Inclusions dispersed in the melt should settle out of it according to Stokes's law:

$$v = \frac{2gr^2(D-d)}{9\eta} \quad (17)$$

where  $r$  = radius of the included particle,

$\eta$  = viscosity of the melt,

$v$  = terminal velocity with which the particle falls or rises,

$D$  = density of the metal,

$d$  = density of the included material,

$g$  = gravitational constant.

Calculations based on Stokes's law suggest that, even in the case of aluminium alloys, where the density of the included material is not very different from that of the basis metal, most inclusions should separate out quickly. For example, with pure aluminium, included particles whose radius is greater than about 0.1 mm. should fall at the rate of 1 mm./sec., so that a dispersion of oxide particles of this size should separate out of a tranquil melt within a few minutes unless the melt is particularly deep. However, this does not take into account the effect of convection currents in the melt, which might be expected to prevent settling out of all but large included particles. Nevertheless, the work of Emley<sup>118</sup> suggests that most kinds of inclusions do in fact settle out of magnesium alloy melts quite quickly, and various authors have reported similar results with other metals. It is, however, not yet clear that settling out can be regarded as a reliable method of removing dispersed inclusions.

The inclusions which arise when zirconium is introduced into magnesium melts in certain ways, in particular when attempts are made to introduce this element by plunging chlorozirconates or zirconium tetrachloride, are inclined to form a persistent dispersion in the melt.<sup>119</sup> The extreme persistence of this type of inclusion, which appears to be unique, is illustrated by the fact that the suspended particles are not removed by normal remelting or by flux-refining processes. The included particles in this case consist of the reaction product (magnesium chloride + sodium chloride from sodium chlorozirconate) trapped in clusters of insoluble zirconium-rich particles; these latter are compounds of zirconium with the "alloying-inhibitor" elements aluminium, silicon, iron, manganese. Care must be taken to avoid this type of inclusion when making alloying additions by reaction between the melt and molten salts.

The elimination of inclusions is assisted by the use of flux covers, a method which is essential with magnesium alloys and is frequently used with aluminium alloys. Fluxes are of two general types—fluid and inspissated. The former are not in fact used to remove inclusions, but rather to prevent their formation in the early stages of

melting. Inspissated fluxes contain thickening agents, in particular magnesium and calcium fluorides, which render skimming and separation of the flux from the metal easy. A further advantage of inspissated fluxes is that there is little danger of the flux being poured into the casting with the metal, since the flux remains as a crust in the crucible. An important function of the flux is, of course, to trap inclusions brought up to the surface of the metal as the result of thermal currents or stirring, and the evidence obtained from magnesium and aluminium alloys suggests that such inclusions are generally rapidly removed in this way from the melt. The action of fluxes has recently been examined by several workers,<sup>118-120</sup> and it appears that fluxes do not generally decompose or react with inclusions to any marked extent; their action is mainly a physical one, the flux wetting the inclusions and causing them to float into the flux layer.

chosen for this purpose is necessarily sensitive to composition rather than to other factors such as gas content, and may therefore be of little use for control of melt quality, though capable of detecting undesirable impurities and incorrect alloying and heat-treatment. The composition of certain alloys (e.g. high-tensile brass) may be estimated from the appearance of the fracture of chill-cast bars.<sup>108</sup>

The difference between the properties of the casting and those of the test-bar is not quite so marked with test-bars designed to give a check on melt quality; these bars should be sensitive to: (i) the presence of inclusions, (ii) gas content, and (iii) in certain alloys, grain-refining treatment. When the melt quality is good, the properties of the bar should be consistently high (though it must be remembered that gas-free metal may not be suitable for poorly fed castings). Provided that these conditions

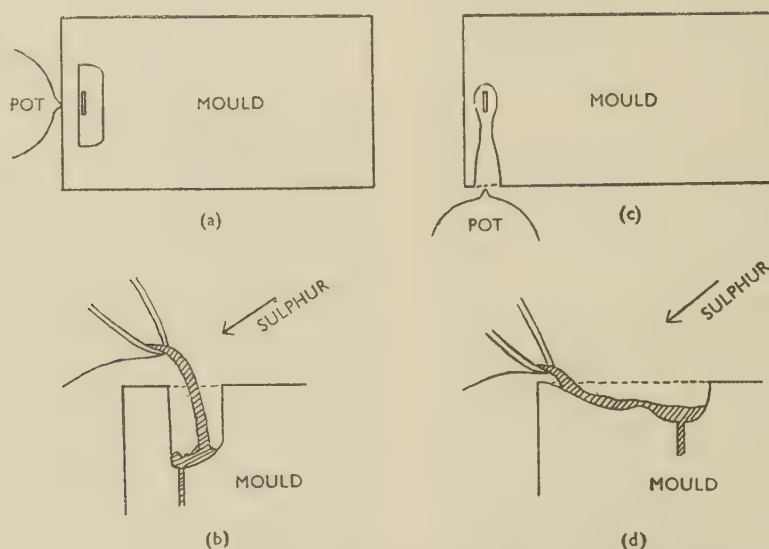


FIG. 24.—Pouring Method Recommended for Magnesium Alloy Sand Castings.

Method commonly adopted  
(a) plan; (b) elevation.

Method involving much reduced risk  
of oxide skins in the casting:  
(c) plan; (d) elevation.

A further advantage of flux treatment is that metal losses are substantially reduced. Recent work on copper alloys has shown that appropriate fluxing treatments will reduce metal losses during the melting of high-tensile brass in crucible furnaces from about 2.7% to less than 0.5%.<sup>121</sup>

#### 4. TEST-BARS FOR CONTROL OF MELT QUALITY

There are still considerable differences of opinion on test-bar design, many of which are due to failure to differentiate between the partly conflicting functions of the test-bar. Some of this confusion may arise because it is supposed that the properties of a casting are identical with those of a test-bar cast from the same melt. In fact, the properties of the casting, which depend upon section thickness and other factors, may bear little relation to those of the test-bar. This is particularly true of bars designed to show the mechanical properties of which the alloy is capable, the properties of the casting often being considerably inferior. The type of bar

are satisfied, the precise design of the test-bar may be chosen to simplify the machining required before testing.

For aluminium alloys, the D.T.D. bar is generally satisfactory, solidifying slowly enough to allow dissolved gas to be evolved and form porosity. The more carefully poured E-bar is often used for alloys containing magnesium; the higher properties obtained may be ascribed partly to greater freedom from inclusions, but they are also attributable to the higher freezing rate and consequently lower sensitivity to gas content of the cast-to-shape bar.

No satisfactory test-bars exist for bronzes and gun-metals. French<sup>108</sup> has shown that consistently high properties may be obtained from test-bars in these alloys only when the pouring conditions are such that a columnar macrostructure is obtained; considerable porosity can be tolerated in such bars because the voids are concentrated at the centre-line and are relatively harmless, but for this reason the properties are not sensitive to gas content. Bars with equiaxial structures, on the other



hand, are more sensitive to gas content, but even the traces of porosity in virtually gas-free metal prevent the highest properties being obtained. With most test-bar designs the occurrence of columnar or equiaxial structures is capricious, owing to variations in pouring speed, temperature, &c., and consequently the tensile properties are notably inconsistent. Certain designs have been recommended<sup>122</sup> because it is possible to obtain with them a consistent series of bars of columnar structure and therefore high tensile properties, but it is hardly surprising that such test-bars have been found to be inadequately sensitive to gas content.<sup>122</sup> Further work on test-bars in gun-metals and bronzes is clearly required. It may prove most convenient to make separate test-pieces for the measurement of gas content and mechanical properties, using for the latter a cast-to-shape bar sensitive to the presence of inclusions but not of gas; this procedure would enable the specified tensile properties to be attained—showing the composition and cleanliness of the metal to be satisfactory—when it is necessary to pour gassy metal for poorly fed castings.

In addition to the types already mentioned, cast-on bars are sometimes advocated. These bars cannot be recommended because their freezing conditions are variable, making them unsuitable for melt control, and are in any case not the same as those in the casting; they may therefore possess quite different mechanical properties.

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# THE METALLURGICAL CONTROL OF QUALITY IN THE PRODUCTION OF COPPER-BASE ALLOY CASTINGS\*

1750

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## SYNOPSIS

The paper deals with those copper-base alloys most commonly used for making castings, i.e. alloys included in British Standard Schedule 1400. Although brief mention is made of chill casting, the paper is principally concerned with sand casting. Before the ranges of alloys and the properties upon which they depend for their service applications are considered, the constitution and the effects of composition and structures on properties are discussed. The influence of impurities and reducing gases is dealt with separately, and then the control of metal quality is described in a section on alloying and melting practice. This is followed by a discussion of tests for metal quality. The modes of solidification of the two groups into which these alloys fall are considered, and a final section is devoted to the control of casting quality, in which reference is made to factors such as feeding and gating, but not to metal quality.

## I.—INTRODUCTION

CONSIDERATION of the metallurgical factors which influence the quality of castings is the function of the works metallurgist from the time an enquiry or order is received, and it is essential that he shall be conscious of the economic aspects of the problems with which he is confronted. He must be able to work with his commercial colleagues to achieve a realistic balance between the technical and the purely economic approaches to what is a satisfactory standard of quality. It is uneconomic to make castings of unnecessarily high quality, but it is highly undesirable to take chances with quality. This balancing of quality with economics—which is the essence of the modern foundry business—can lead to many metallurgical and foundry problems that would otherwise not exist. Thus, the use of secondary materials is frequently necessary for economic reasons but can bring technical problems in its train; likewise present-day technical-economic factors tend to prejudice normal good foundry practice, as, for example, when the necessity to crowd castings into a small moulding box leads to foundry problems.

The author is aware of the ambiguity that arises from the expressions “quality of castings”, “casting quality”, “control of quality”, and “quality control”, and it may therefore be helpful to give his interpretations of them at the outset. The “quality of a casting” or “casting quality” embraces metal quality and the degree of imperfection with regard to physical characteristics. Metal quality depends on chemical composition, which includes basic composition and impurities, and microstructure, which is influenced by composition and rate of cooling. Imperfection in physical

characteristics, in the present sense, refers to unsoundness, inclusions, cracks, and dimensional inaccuracy, and faults in surface finish. By “control of quality” is meant the use, throughout the various stages of a process, of manufacturing procedures designed to achieve a given standard of quality, including those steps based upon the interpretation of “quality-control” test results. “Quality control” is interpreted as the application of suitable tests at a predetermined rate for the purpose of maintaining a required standard of quality at any stage of manufacture, and the analysis and interpretation of those results.

Sand castings are produced in a large number of copper-base alloys, some of which are not widely known and would require special consideration; die-castings are necessarily made from a limited number of alloys. Most of the castings used in industry are made from alloys based on copper-tin, copper-zinc, or copper-aluminium, and it is with these that the paper is concerned; in particular, reference is made to the most popular alloys, i.e. those included in British Standard Schedule 1400.<sup>1</sup> ‡

In discussing the control of the quality of a casting, those properties must be considered on which the casting will depend for its suitability for the application for which it is intended. Before defining the alloys used in practice, it is therefore necessary to discuss constitution and the influence of basic composition and microstructure on properties; this also enables the effects of inadequacy of control over these factors to be assessed. Similarly, a section on mode of solidification leads up to the final section on the control of casting quality, which deals with factors other than metal quality.

While metal quality depends essentially upon basic composition and microstructure, it is affected by the

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‡ At the time of writing, B.S. Schedule 1400 is under revision.

In order that the paper may be of as much value as possible, the alloys are quoted in accordance with the revised version, in anticipation either that the revision will be approved or that no major alteration will be introduced affecting the nomenclature or basic compositions of the alloys involved.

presence of impurities, which logically include gases. The influence of reducing gases, particularly on the copper-tin alloys, is, however, of such significance that a separate section is devoted to this subject. Another section is allocated to alloying and melting practice, upon which control of metal quality largely depends.

Tests used for the quality control of metal are discussed, but those factors which principally affect surface finish and dimensional accuracy of castings fall outside the scope of the paper, and the non-destructive techniques for the detection of inclusions, cracks, and unsoundness of various types are considered in a separate contribution.\* The application of statistics to quality control is also dealt with elsewhere.†

Because of the number of alloys of various types concerned and the wide scope of the subject, it is possible to refer only briefly to the various theoretical and practical considerations involved. An endeavour has been made, however, to include reference to the literature thought to be of most value to the works metallurgist concerned with controlling the quality of cast copper-base alloys. Clearly, comment cannot be offered on the whole of the literature to which reference is made, and it should not be assumed that the author necessarily shares the views expressed.

At this stage it is convenient to refer to literature of a scope too broad for inclusion under the individual sections of the paper. A recently published book edited by Murphy<sup>2</sup> on "Non-Ferrous Foundry Metallurgy" covers a wide field through the co-ordinated contributions of a number of specialists. American practice and experience are described in "Copper-Base Alloys Foundry Practices",<sup>3</sup> the second edition of which was published in 1952, and in a publication "Process Control of Brass and Bronze Foundry Procedure",<sup>4</sup> issued in 1949. A book by R. F. Hudson<sup>5</sup> has a practical bias and covers the sand casting and chill casting of all the copper-base alloys normally used. Hanson and Pell-Walpole's book<sup>6</sup> deals with both theory and practice concerning the properties and manufacture of chill-cast copper-tin alloys; while "The Relationship between Pouring Temperature, Porosity, and Tensile Strength of Sand-Cast Bronze" is discussed by Pell-Walpole in a separate paper.<sup>7</sup> A series of articles by Hinchcliffe<sup>8</sup> on running and feeding practice for copper-tin alloys has recently appeared, and earlier a similar series by Reid<sup>9</sup> dealt with the aluminium bronzes and high-tensile bronzes.

## II.—CONSTITUTION

### 1. COPPER-TIN ALLOYS

Alloys of copper and tin are not normally cast without the addition of phosphorus or zinc, but the fundamental characteristics of the alloys in common use based on copper-tin are those of the copper-tin system.

The constitution of the binary and ternary copper-tin systems has been fully discussed by Hanson and Pell-Walpole.<sup>6</sup> The latest copper-tin diagram is that due to Raynor.<sup>10</sup> Under equilibrium conditions, alloys containing up to about 16% tin are all- $\alpha$  at 500° C., and without prolonged annealing this structure persists down to room temperature.

Because of the long solidification range, with rates of

cooling normally encountered in practice, the  $\alpha$  phase is heavily cored, and in effect the solidus is moved in the direction of reduced tin concentrations. With alloys containing up to about 7% tin, little or no  $\beta$  is formed in the peritectic reaction at 798° C., and the final structure consists of cored  $\alpha$ . With increase in tin content  $\beta$  and  $\gamma$  are formed, with the effect of still further extending the solidification range. At 520° C. the eutectoid ( $\alpha + \delta$ ) is formed, and no further change takes place, so that the final structure found in practice, in alloys containing more than about 7% tin, is ( $\alpha + \delta$ ) eutectoid in a matrix of cored  $\alpha$  solid solution.

#### (a) Copper-Tin-Phosphorus Alloys

The most recent work on the copper-tin-phosphorus system is that by Verö,<sup>11</sup> and sections due to him, with tin constant at 5 and 10% and with phosphorus constant at 1%, are shown in Fig. 1. The two most interesting features of these diagrams are that the maximum solid solubility of phosphorus decreases as the tin content is raised, and that a eutectic is formed at 637° C. With increase in phosphorus there is therefore a marked widening of the solidification range, and the effect of this even at very low contents of phosphorus might prove to be an important factor which has not been given sufficient consideration. Additions of phosphorus above about 0.15% are sufficient to give rise to the formation of the  $\text{Cu}_3\text{P}$  constituent, with the effect of prolonging the solidification range, e.g. in an alloy containing 10% tin from approximately 270° C. in the absence of phosphorus to 390° C. with more than 0.15% phosphorus. Only those alloys containing sufficient phosphorus to develop the  $\text{Cu}_3\text{P}$  phase can logically be referred to as phosphor bronzes, and these solidify with cored  $\alpha$  solid solution ( $\alpha + \beta + \text{Cu}_3\text{P}$ ) being formed at the eutectic point at 637° C.; ( $\alpha + \gamma + \text{Cu}_3\text{P}$ ) at 587° C.; and finally ( $\alpha + \delta + \text{Cu}_3\text{P}$ ) at 500° C. With insufficient tin present to form the  $\delta$  phase,  $\alpha$  and  $\text{Cu}_3\text{P}$  are the final phases. The structure normally found in cast phosphor bronzes is the ( $\alpha + \delta + \text{Cu}_3\text{P}$ ) complex in a cored  $\alpha$  matrix.

#### (b) Copper-Tin-Zinc Alloys

The original work on the ternary copper-tin-zinc system was carried out by Hoyt;<sup>12</sup> subsequent work has been published by Tammann and Hansen<sup>13</sup> and Bauer and Hansen.<sup>14</sup> Most of Hoyt's work has been confirmed, although some modification has been made to the composition of the  $\alpha$  phase at the solidus. Tammann and Hansen determined the limit of the  $\alpha$  solubility range, as shown by the line *ab* in Fig. 2; the line *ef* is an approximation for the limit of ternary  $\alpha$  in chill-cast alloys, given by Hanson and Pell-Walpole.<sup>6</sup> In practice the structures of these alloys whose compositions lie normally between 3% tin, 12% zinc and 12% tin, 2% zinc can be interpreted by consideration of the copper-tin system, taking 2% zinc as equivalent to 1% tin. The  $\delta$  phase first occurs in sand-cast alloys having a tin equivalent of about 7%.

#### (c) Copper-Tin-Zinc-Phosphorus Alloys

The copper-tin-zinc-phosphorus alloys can be considered in terms of the ternary copper-tin-phosphorus system, using the tin equivalent of zinc.

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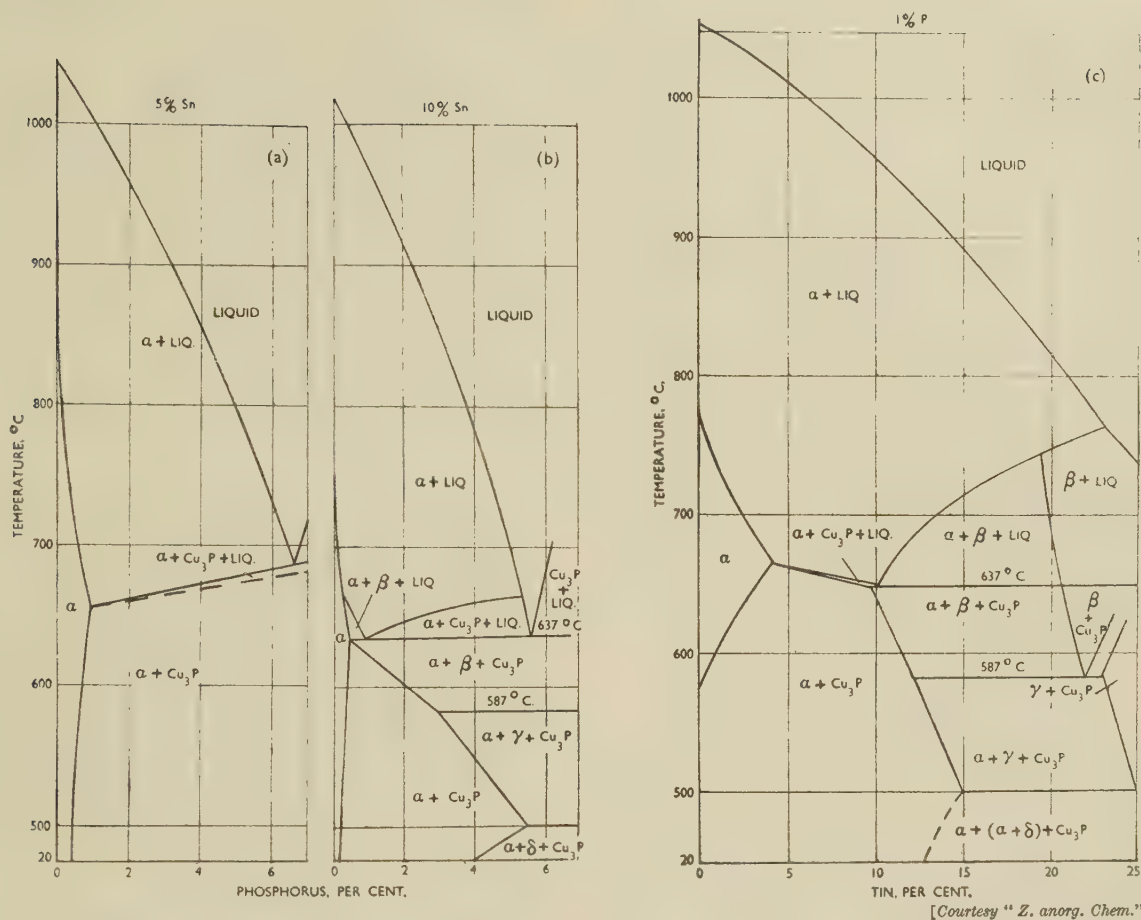


FIG. 1.—Vertical Sections of the Copper-Tin-Phosphorus System. (a) Sn constant at 5%; (b) Sn constant at 10%; (c) P constant at 1%. (Verö,<sup>11</sup>)

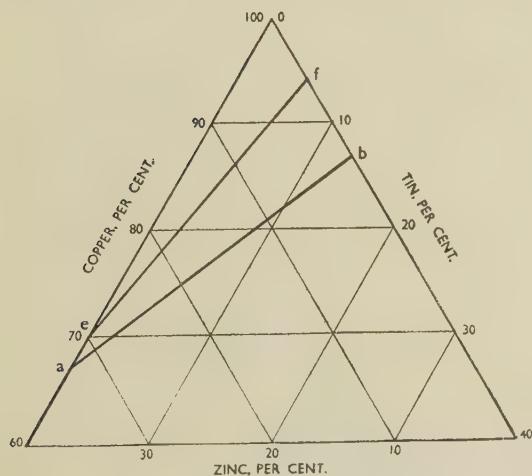


FIG. 2.—Liquidus of Copper-Tin-Zinc Alloys. Line  $ab$  = limit of  $\alpha$  solubility range. (Tammann and Hansen.<sup>13</sup>) Line  $ef$  shows approximation for limit of ternary  $\alpha$  in chill-cast alloys. (Hanson and Pell-Walpole.<sup>6</sup>)

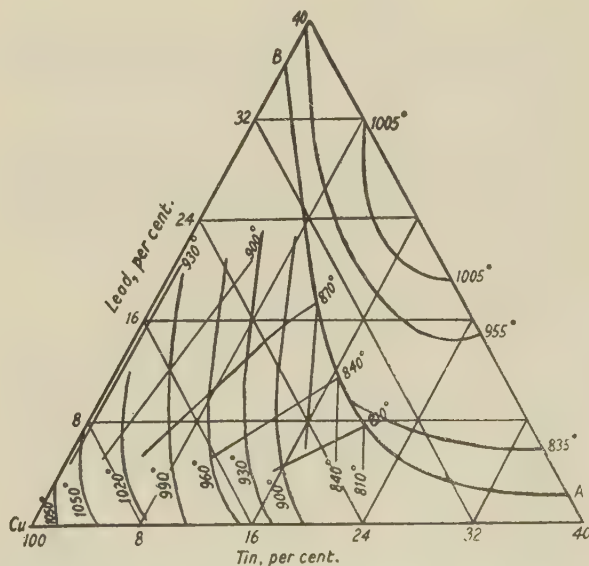


FIG. 3.—Liquidus and Separation Surfaces of the Copper-Tin-Lead System. (Hanson and Pell-Walpole.<sup>6</sup>) [Courtesy Edward Arnold and Co.]

(d) *Copper-Tin-Lead and Copper-Tin-Zinc-Lead Alloys*

Lead is virtually insoluble in copper-base alloys, and is retained with the last liquid to solidify, finally itself solidifying at 327° C.

There is a range of immiscibility in the alloys containing between 36 and 92% lead, and in the copper-lead system, with increase in lead content, the liquidus drops from 1083° C. at 0% lead to 954° C. at the limit of miscibility at 36% lead. Hanson and Pell-Walpole<sup>6</sup> have published a composite diagram (Fig. 3) for copper-tin-lead which draws attention to the variation of the limit of miscibility with tin content (line *AB*) and indicates the maximum lead:tin ratio with which an alloy free from segregation can be produced by ordinary casting methods. This is important in the case of only one type of lead bronze normally used, in which lead exceeds 20% and tin exceeds 4%. In normal practice it is found that there are critical values rather below those given in the diagram which it is unwise to exceed if immiscibility is to be avoided; for example, with 25% lead not more than 5% tin should be included.

Copper-tin-zinc-lead alloy structures can be interpreted in terms of the copper-tin-lead system using the tin equivalent of zinc.

(e) *Copper-Tin-Lead-Phosphorus and Copper-Tin-Zinc-Lead-Phosphorus Alloys*

Hanson and Pell-Walpole<sup>6</sup> studied the influence of phosphorus on alloys containing copper-tin-lead and copper-tin-zinc-lead, and found that it seriously reduces the range of complete miscibility. They quote as an example that whereas an alloy containing 6.5-8.5% tin, 2% zinc, and 2-5% lead can be cast successfully with up to 0.6% phosphorus, with 1% phosphorus the liquid alloy separates.

## 2. COPPER-ZINC ALLOYS

The alloys of copper and zinc are known as brasses, while the high-tensile brasses are derived from these by the addition of various elements which improve the strength, in some cases by promoting grain refinement. The influence of the added elements on the microstructure can be simply but broadly interpreted in terms of the copper-zinc diagram by the use of Guillet's zinc equivalents.<sup>15</sup> The values normally adopted are given in Table I. The principle involved depends upon the

TABLE I.—Zinc Equivalents.

	Added to Zinc, %	Added to Copper, %
Aluminium . . . . .	6.0	...
Tin . . . . .	2.0	...
Iron . . . . .	0.9	...
Manganese . . . . .	0.5	...
Lead . . . . .	1.0	...
Nickel . . . . .	...	1.3

movement of the solubility limits, as indicated by the  $\alpha/(\alpha + \beta)$  and  $(\alpha + \beta)/\beta$  boundaries, towards increased copper by an amount constant for each element, known as the "zinc equivalent", proportional to the amount

of the element included. This is approximately true within certain limits for each element, depending upon the constitution of the alloy system.

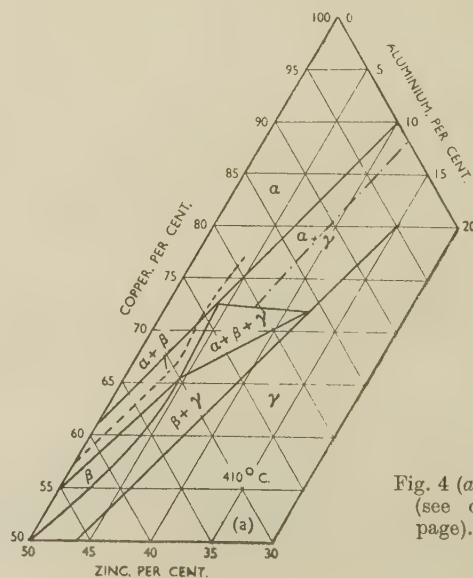
The latest diagram of the binary system is due to Raynor.<sup>16</sup> In the composition range of the cast brasses, the alloys with lower zinc content form only the  $\alpha$  phase and cool with cored  $\alpha$  structures, while in alloys of higher zinc content a peritectic reaction occurs at 902° C. between  $\alpha$  and liquid to yield the  $\beta$  phase. With zinc contents of the order of 40% or above, the alloys solidify as  $\beta$ , and when the zinc content does not exceed 46%,  $\alpha$  is precipitated from the solid  $\beta$  at a temperature dependent upon the composition of the alloy. The high-tensile brasses used in practice fall within this range. With still higher zinc content, a peritectic reaction takes place at 834° C. between  $\beta$  and liquid to form the harmful  $\gamma$  phase. The  $\beta \rightarrow \beta'$  disorder/order transformation at 454° C. is not normally significant in practice.

(a) *Copper-Zinc-Aluminium Alloys*

Information on this system is due to Bauer and Hansen;<sup>17</sup> sections are shown in Fig. 4.

While aluminium is added to brass in amounts up to about 0.25% to promote fluidity, as an alloying addition for the improvement of properties about 1% or more is normally added. In the high-tensile brasses of lower tensile strength (28-38 tons/in.<sup>2</sup>) aluminium additions are generally made of up to 2-2½%, whereas in the alloys of higher strength (above 38 tons/in.<sup>2</sup>), additions are normally of the order of 5%. The peritectic temperature (902° C.) of the copper-zinc system is progressively raised by additions of aluminium, and the solubility limits of the  $\alpha$  and  $\beta$  phases of the copper-zinc solid solution are displaced towards higher copper concentrations.

Isomorphism exists between the respective  $\alpha$ ,  $\beta$ , and  $\gamma$  phases of the copper-zinc and copper-aluminium systems. The sections in Fig. 4 show that at 5% aluminium under equilibrium conditions the  $\gamma$  phase would appear in  $\alpha/\beta$  and  $\beta$  alloys, separating at a temperature below 550° C., but with normal rates of cooling  $\gamma$  does not appear in the microstructures of those alloys used in practice.

Fig. 4 (a)  
(see opposite  
page).



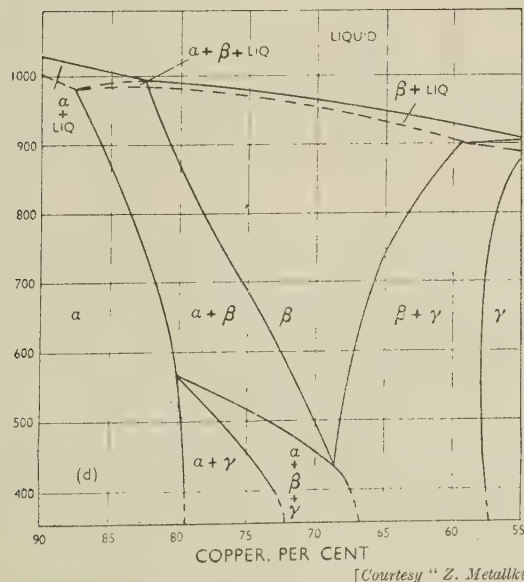
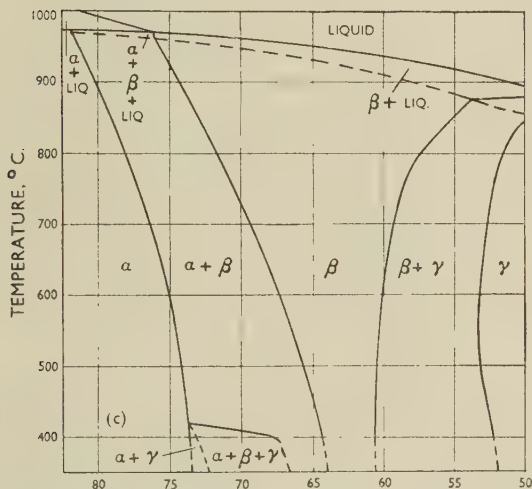
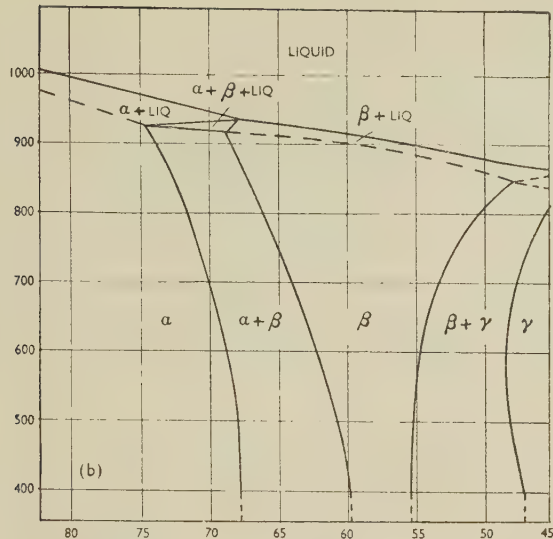
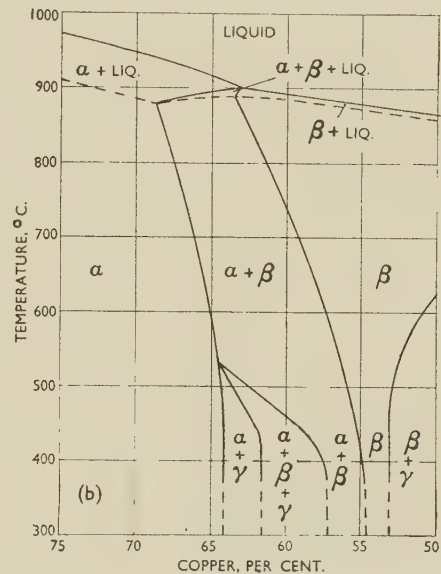
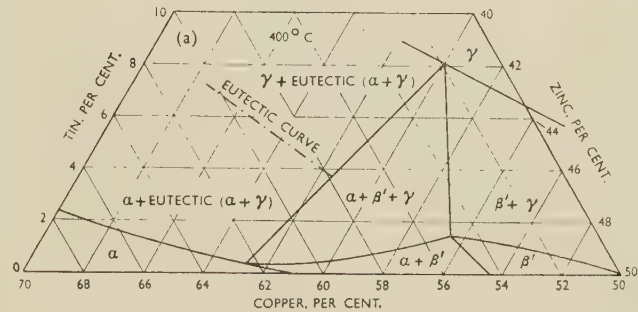


FIG. 4.—The Copper-Zinc-Aluminum System. (a) Horizontal section at 410°C. (b)–(d) Vertical sections: (b) Al constant at 2%; (c) Al constant at 4%; (d) Al constant at 6%. (Bauer and Hansen.<sup>17</sup>)

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### (b) Copper-Zinc-Tin Alloys

Bauer and Hansen<sup>14</sup> also studied this system, and sections are shown in Fig. 5. The  $\alpha$  and  $\beta$  solid solutions of the binary systems copper-zinc and copper-tin are



[Courtesy "Z. Metallkunde."]

FIG. 5.—The Copper-Zinc-Tin System. (a) Horizontal section at 400°C. (b) Vertical section with tin constant at 1.05%. (Bauer and Hansen.<sup>14</sup>)

isomorphous, and the peritectic temperature (902°C.) of the copper-zinc system is progressively lowered by increased additions of tin; at 1% the decrease is of the order of 25°C. The solubility limits of the  $\alpha$  and  $\beta$  phases are displaced towards higher copper concentrations with increase in tin content, and the width of the  $(\alpha + \beta)$  field is considerably narrowed. In alloys of lower zinc content some or all of the  $\beta$  phase decomposes to  $(\alpha + \gamma)$ . Above 1.5% tin at 400°C. the  $\gamma$  phase always occurs between 54 and 64% copper, and for this reason in practice tin is rarely allowed to exceed 1.2%. Tin in these alloys can have a marked effect on susceptibility to inverse segregation and on the brittleness of the segregate, owing to the possible formation of the  $\gamma$  phase.

### (c) Copper-Zinc-Iron Alloys

In addition to the work of Bauer and Hansen,<sup>18</sup> Child<sup>19</sup> has considered the effects of iron on the copper-zinc system. The influence of iron on the alloys in the range normally used in practice is shown in Fig. 6, due to Bauer and Hansen. The solubility of iron in the  $\alpha$

and  $\beta$  phases is similar to that in copper and greatly increases with temperature. According to Bauer and Hansen, the peritectic reaction ( $\alpha + \text{liquid} \rightleftharpoons \beta$ ) takes

increase in the liquidus temperature, as in the copper-iron system, and the iron appears in the form of a primary iron-rich phase.

In practice, with the high-tensile brasses, the iron-rich primary phase is found in alloys containing down to 0.7% iron, which is the minimum amount necessary for grain refinement; in alloys containing aluminium, however, consideration has to be given to the effect that this element has on the solubility of iron. The iron-rich phase usually appears as a small bluish-grey constituent, when specimens are etched with ammoniacal reagents, taking the form of primary or secondary globular particles, rosettes, needles, or irregularly shaped particles, which should preferably be well distributed but which can occur in groups or aggregates.

#### (d) Copper-Zinc-Manganese Alloys

The main work in this field has been carried out by Bauer and Hansen.<sup>20</sup> Manganese in the amounts normally added (up to 3%) does not have any marked effect on the copper-zinc system, save that of moving the phase boundaries slightly towards lower copper concentrations with increase in manganese, and no new phases are formed. The phases reported by Child,<sup>19</sup> which, as he points out, do not correspond with any phases reported by Bauer and Hansen, are undoubtedly attributable to impurities introduced with the manganese. The temperature of the beginning of crystallization of the  $\beta$  phase is decreased by the addition of manganese and the solidification range gradually widened. Child reports that the introduction of manganese raises the temperature at which the primary iron-rich phase begins to separate.

#### (e) Copper-Zinc-Nickel Alloys

The system has been studied by Bauer and Hansen.<sup>21</sup> The  $\alpha$  and  $\beta$  phases of the copper-zinc system are isomorphous with those of the nickel-zinc system, and the peritectic temperature of the copper-zinc system is only slightly raised by additions of nickel. With increase in nickel, the phase fields of the copper-zinc system are displaced in the direction of lower copper concentrations, and no new phase is formed. This rather simple consideration of the ternary system is complicated by the fact that high-tensile brasses containing nickel may also contain aluminium or tin, so that new phases can be formed.

#### (f) Copper-Zinc-Silicon Alloys

The system has been investigated by Gould and Ray<sup>22</sup> and by Vaders.<sup>23</sup> Silicon is not normally an addition in the conventional high-tensile brasses, but is present as an impurity which goes into solution in the iron-rich constituent and the  $\alpha$  and  $\beta$  phases.

#### (g) Copper-Zinc-Lead Alloys

This system has been examined by Bauer and Hansen.<sup>24</sup> Lead is virtually insoluble and solidifies in the form of particles finely dispersed throughout the structure.

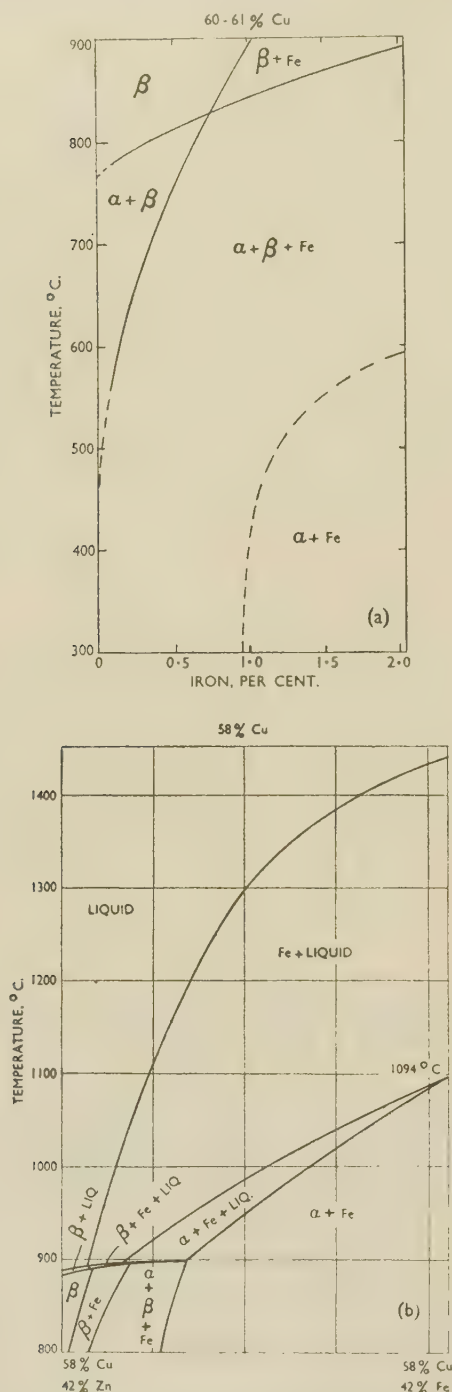


FIG. 6.—Vertical Sections of the Copper-Zinc-Iron System. (a) Cu constant at 60-61%; (b) Cu constant at 58%. (Bauer and Hansen,<sup>18</sup>)

place within a narrow temperature interval, and begins at a temperature only a few degrees below that of the copper-zinc system. With copper less than 70% and with more than about 1% iron present, there is a sharp

### 3. COPPER-ALUMINIUM ALLOYS

The binary alloys of copper and aluminium are not normally used for the manufacture of sand castings for



the reason given below, but it is necessary to consider the binary copper-aluminium diagram before referring to the alloys used in practice. The latest diagram is due to Raynor.<sup>25</sup> The important features are the narrow solidification range; the eutectic point at 1037° C., 8.5% aluminium; and the eutectoid reaction, which occurs at 565° C., when the  $\beta$  phase breaks down to ( $\alpha + \gamma_2$ ). This breakdown can occur with slow rates of cooling such as are normally experienced in heavy sections in sand castings. This effect, which has become known as "self-annealing", results in embrittlement, and for this reason binary copper-aluminium alloys are rarely used in practice for sand casting. The embrittlement is normally counteracted by the addition of iron to the alloy.

In practice, alloys with as little as 8% aluminium produce a duplex structure in which the  $\beta$  phase is retained, but in the absence of iron this would break down as

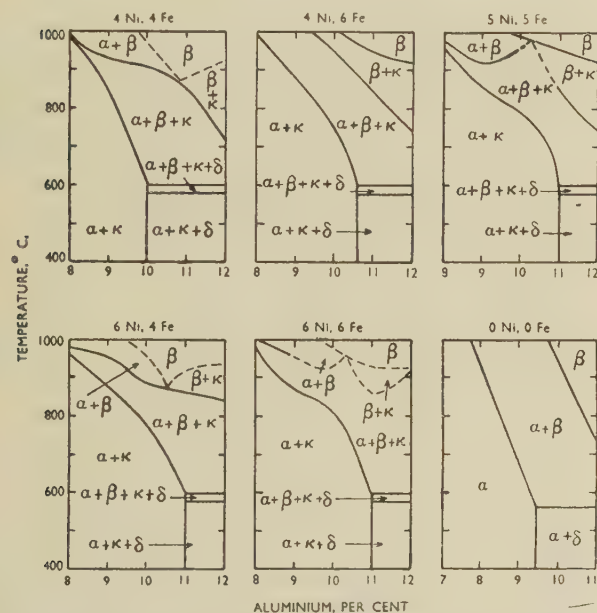


FIG. 7.—The Approximate Relationship Between Composition, Temperature, and Phase Fields in Copper-Aluminium-Nickel-Iron Alloys. Sections at constant nickel and iron contents. (Cook, Fentiman, and Davis.<sup>29</sup>)

described. The straight copper-aluminium alloys are used only in die-casting, where the rate of cooling is sufficiently rapid to suppress the eutectoid transformation.

#### (a) Copper-Aluminium-Iron Alloys

Work on the influence of iron on the eutectoid transformation has been reported by Kasberg and Mack.<sup>26</sup> Iron speeds up the eutectoid transformation without appreciably affecting the transformation temperature, and according to Bradley and Goldschmidt,<sup>27</sup> with aluminium contents up to 20%, 2% iron is retained in the  $\alpha$  solution. Additions of iron in excess of 2% give rise to the formation of a complex compound which is distributed throughout the structure and has a grain-refining effect. According to Dreher,<sup>28</sup> the effective aluminium content is reduced by 0.12–0.39% per 1% of iron added, according to the manner in which the iron is introduced into the alloy.

Taking into account the features described, the structures of the copper-aluminium-iron alloys used in practice can be broadly interpreted in terms of the copper-aluminium diagram.

#### (b) Copper-Aluminium-Nickel-Iron Alloys

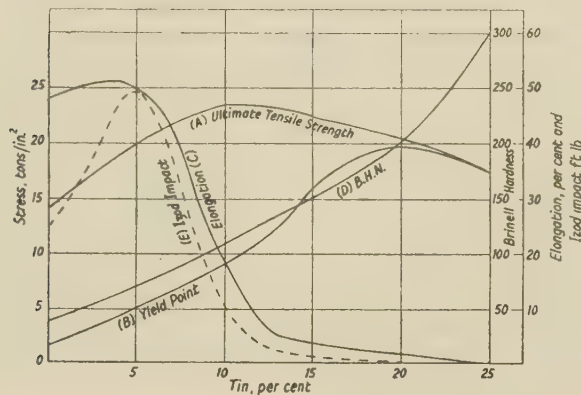
It was only recently that any information on this complex system was published, in a paper by Cook, Fentiman, and Davis.<sup>29</sup> A series of diagrams from this paper is reproduced in Fig. 7, showing sections at constant nickel and iron contents, which give the approximate relationship between composition, temperature, and the phase fields. The alloys normally used in practice first solidify as all- $\beta$ , although very occasionally primary particles of an iron-rich phase have been observed. The individual  $\alpha$  and  $\kappa$  phases separate from  $\beta$ , the first to appear being dependent upon the precise composition; and at lower temperatures, also dependent upon the precise composition, the  $\beta$  breaks down to ( $\alpha + \kappa$ ) to give a phase of eutectoidal appearance. The final structure, therefore, consists of  $\alpha$  grains bounded by ( $\alpha + \kappa$ ), with small particles of  $\kappa$  as first precipitated from the  $\beta$ , dispersed throughout. With very slow rates of cooling, such as might arise in very large castings, the ( $\alpha + \kappa$ ) phase coarsens very considerably, with a marked adverse effect on the properties.

### III.—THE INFLUENCE OF BASIC COMPOSITION AND MICROSTRUCTURE ON PROPERTIES

#### 1. COPPER-TIN ALLOYS

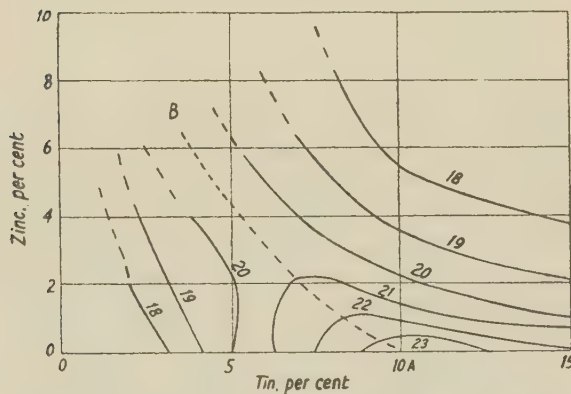
The mechanical properties of the sand-cast copper-tin alloys, in addition to being governed by the basic composition and affected by impurities, are influenced by factors which affect the gas content of the metal and the mode of solidification, making it difficult to control the variables so that consistent results can be obtained. Probably because of these difficulties few reliable data are available on the influence of composition on the mechanical properties of sand-cast alloys. Hanson and Pell-Walpole<sup>6</sup> have, however, made a study of the effects on the mechanical properties of chill-cast alloys of variations in composition, which can be made under carefully controlled conditions, and a paper has been published by Le Thomas in which he considers the relationship between microstructures and mechanical properties.<sup>30</sup> In both sand- and chill-cast materials, with increase in the proportion of the ( $\alpha + \delta$ ) eutectoid, or in  $\text{Cu}_3\text{P}$ , tensile strength increases up to the point at which networks of the phases are unavoidably formed, causing the strength to drop. Increases in either of these phases also result in increase in proof stress and hardness (the  $\delta$  phase is the harder), but marked reduction in ductility and impact resistance. Owing to the higher rates of cooling in chill casting, more of the ( $\alpha + \delta$ ) eutectoid is formed at a given composition, and it follows that rather higher additions of tin, zinc, or phosphorus are necessary in sand-cast alloys to produce equivalent effects. Hanson and Pell-Walpole<sup>6</sup> state that with chill-cast binary tin bronzes the maximum tensile strength is reached at 10% tin, which they regard as the limiting tin content above which the continuous intercrystalline network of the ( $\alpha + \delta$ ) eutectoid is formed. Proof stress also increases

with higher tin content, and continues to rise with further increase above 10% to a maximum at 17–20% tin. The tensile strength, however, falls, and beyond this tin level the two values become virtually identical. Hardness also rises with increase in tin content. The elongation values become greater with increase in tin up to about 5%, at which stage the ( $\alpha + \delta$ ) eutectoid appears, and elongation then falls to about 3% at 12% tin and to zero at about 25% tin. Izod impact values follow a similar trend, dropping to 5 ft.-lb. at 10% tin.



[Courtesy Edward Arnold and Co.]

FIG. 8.—Mechanical Properties of Chill-Cast Tin Bronzes. (Hanson and Pell-Walpole.<sup>6</sup>)



[Courtesy Edward Arnold and Co.]

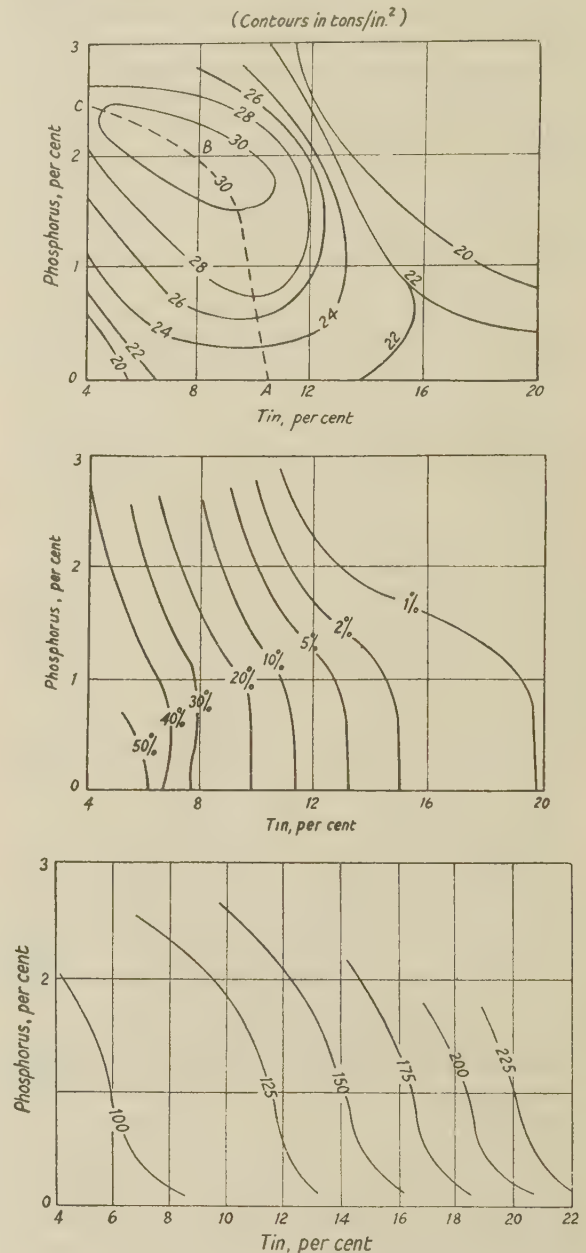
FIG. 9.—Tensile Strength (tons/in.<sup>2</sup>) of Chill-Cast Zinc-Tin Bronzes. (Hanson and Pell-Walpole.<sup>6</sup>)

Fig. 8 is taken from the work of Hanson and Pell-Walpole.<sup>6</sup>

With increase in zinc content, the amount of tin necessary to produce maximum strength is reduced. According to Hanson and Pell-Walpole,<sup>6</sup> and to an earlier paper by Winterton,<sup>31</sup> owing to the adverse influence of zinc on fluidity and soundness in chill casting, strength and ductility are appreciably lower than in binary copper-tin alloys for a given proportion of ( $\alpha + \delta$ ) eutectoid in the structure (Fig. 9). This is not necessarily true, however, in sand casting, where other factors are involved.

Phosphorus up to about 0.7–0.8% does not appreciably affect the ductility of the chill-cast copper-tin alloys, but further additions are significant. Hardness, frequently an important property with these alloys, in-

creases with the addition of either tin or phosphorus. The effect of composition on strength, ductility, and hardness is shown in Fig. 10.<sup>6, 32</sup>



[Courtesy Edward Arnold and Co.]

FIG. 10.—Properties of Chill-Cast Phosphorus-Tin Bronzes. (a) Tensile strength (tons/in.<sup>2</sup>), (b) Elongation values, and (c) Brinell hardness. (Hanson and Pell-Walpole.<sup>6</sup>)

Additions of lead, forming soft unalloyed particles in the structure, reduce strength, ductility, and hardness, though in practice this might be masked by the beneficial effect of lead on soundness.

## 2. COPPER-ZINC ALLOYS

Considering first the basic copper-zinc system, with zinc contents up to nearly 36% the alloys are all  $\alpha$  and of low strength, but at this point, with the rates of cooling



normal to sand castings, the stronger  $\beta$  phase appears, and above 46½% the structure becomes all- $\beta$ : it follows that throughout this range 1% zinc is approximately equivalent to 10%  $\beta$ . With increase in the proportion of  $\beta$  phase, the tensile strength increases but ductility decreases (Table II). With the high-tensile brasses, the

TABLE II.—*Mechanical Properties of Sand-Cast Copper-Zinc Alloys.* (Murphy.<sup>33</sup>)

Zinc, %	$\alpha$ Phase, %	Tensile Strength, tons/in. <sup>2</sup>	Elongation, %	Brinell Hardness No.
33.7	100	15.0	63	55
35.0	88	19.1	59	59
38.0	75	21.5	56	64
40.1	69	23.0	55	72
41.8	55	24.6	50	80
43.7	14	27.8	27	102
45.5	0	30.4	27	105

same considerations apply in terms of zinc equivalent, microstructure, and mechanical properties, but ductility at first increases with increase in  $\beta$ , to a peak at about 30%  $\beta$ , and then falls (Table III).

TABLE III.—*Mechanical Properties of Sand-Cast Manganese Bronze.* (Murphy.<sup>33</sup>)

Zinc, %	$\alpha$ Phase, %	Tensile Strength, tons/in. <sup>2</sup>	Elongation, %	Brinell Hardness No.
31.0	100	20.8	24	72
32.9	78	23.8	36	75
37.5	70	27.2	50	85
39.2	45	30.9	42	95
41.1	25	34.2	28	121
44.1	0	37.2	21	129
47.8	0 *	24.4	4	138

\*  $\gamma$  phase present.

High-tensile brasses of lower strength (HTB 1) are strengthened by the addition of aluminium or tin, frequently of both. A relationship exists between the tin and aluminium additions which makes it necessary to work above minimum limits in order to achieve the strength required, but not to exceed certain combinations of aluminium and tin beyond which the properties are adversely affected. If the tin content is maintained constant at a medium level of, say, 0.5%, and the  $\alpha$ : $\beta$  proportion is also constant, increase in aluminium content results in improved proof-stress and tensile-strength values, with little change in elongation, particularly when aluminium exceeds 1.75%.

In those alloys of medium strength (HTB 2) which are normally made with an addition of about 5% aluminium, it is necessary to regard tin as an impurity. With aluminium present in this proportion, very high strengths can be achieved by the further addition of zinc, up to and beyond the point at which the alloy becomes all- $\beta$  (HTB 3). The  $\beta$  brasses containing a high proportion of aluminium are susceptible to stress-corrosion cracking, and caution has to be exercised in their use. This has been known for nearly fifty years, but recent work by the British Non-Ferrous Metals Research Association and others<sup>34-36</sup> on the metallurgical principles involved

is of interest. Similar properties cannot be obtained by adding tin in amounts sufficient to produce all- $\beta$  structures, or by increasing the zinc contents of those alloys containing the maximum amount of tin, which in practice is about 1.2%. With a nominal tin content of the order of 1%, aluminium in more than very small amounts, up to 0.3%, is undesirable. It has been found that the principal advantage gained by an increase in the tin content is a rise in the proof stress.

The main virtue claimed for the high-tensile brasses of high tin content is the combination of strength with corrosion-resistance, particularly under marine conditions. More recent work by the present author and his colleagues has shown that improved mechanical properties, with equal corrosion-resistance, can be obtained in alloys with lower tin contents; this permits the use of higher additions of aluminium, but it is essential that tin should not be reduced below 0.5% in order to maintain the desired degree of corrosion-resistance.

The principal purpose of the addition of iron is to promote grain refinement, as a result of the separation of the primary iron-rich phase. While manganese has some beneficial effect on mechanical properties, it is not an essential addition in the high-tensile brasses generally, and is not a particularly effective grain refiner, but its presence is desirable in alloys of high aluminium content<sup>37</sup> in view of its stabilizing effect on the  $\beta$  phase. In alloys of lower aluminium content, manganese can be absent or maintained at a low level, and iron present to the extent of 1% is adequate for grain refinement, but in alloys containing more aluminium, e.g. 5%, more manganese and iron contents of the order of 1.5–3% are required.

Lead is normally included to facilitate machining in the ordinary sand-cast  $\alpha$  brasses and sometimes in the high-tensile brasses, but with the latter caution has to be exercised because of the adverse influence on properties. Its presence results in hot shortness, particularly noticeable in die-casting, although a free-machining die-casting alloy has been developed which contains lead.<sup>38</sup>

### 3. COPPER-ALUMINIUM ALLOYS

In the simple aluminium bronzes containing iron, with increase in aluminium content, passing from the  $\alpha$  phase

TABLE IV.—*Mechanical Properties of Aluminium Bronze Containing 3% Iron.* (Murphy.<sup>33</sup>)

Aluminium, %	$\alpha$ Phase, %	Tensile Strength, tons/in. <sup>2</sup>	Elongation, %	Brinell Hardness No.
6.02	100	32.2	52	103
8.42	50	35.6	48	111
10.12	10	40.4	28	137
12.20	Trace	37.4	3	217
13.60	0 *	18.8	1	277
16.0	0 *	...	...	363

\*  $\gamma$  phase present.

through the ( $\alpha$  +  $\beta$ ) range, proof stress, tensile strength, and hardness are increased while ductility falls off. A peak in the tensile strength is reached in the region of the ( $\alpha$  +  $\beta$ )/ $\beta$  boundary, and with further increase in aluminium there is a drop in tensile strength and a marked reduction in ductility, particularly when suffi-

cient aluminium is present for the  $\gamma_2$  phase to appear. Table IV gives the properties of alloys containing 3% iron, as sand cast.

The introduction of nickel to produce the complex alloys has a pronounced effect on the tensile strength, the proof stress, and the fatigue characteristics. In addition, while the aluminium bronzes generally are regarded as being reasonably corrosion-resistant, the complex aluminium bronzes are much superior to the others. Furthermore, they exhibit resistance to fatigue and corrosion-fatigue to a much higher degree than the high-tensile bronzes. They are also reasonably resistant to creep and oxidation at elevated temperatures, and under suitable conditions show considerable resistance to wear.

ably most frequently supplied in the form of solid or cored sticks, and a number of plants are now coming into operation for the production of this alloy in the form of semi-continuously<sup>39</sup> or continuously<sup>40,41</sup> cast sticks and tubes. Another hard phosphor bronze, PB 2, is used principally for gears and has a higher tin content and lower phosphorus content, normally 12% tin and 0.3% phosphorus. These alloys depend for their strength and wear-resisting characteristics on a carefully controlled composition to give the desired structure, i.e. ( $\alpha + \delta + \text{Cu}_3\text{P}$ ) complex well distributed in a matrix of  $\alpha$  solid solution, the distribution being controlled by casting conditions.

When a softer alloy is required, one of the lead bronzes

TABLE V.—Typical Mechanical Properties of Aluminium Bronzes.

	BB11 * and A.S.T.M. B148								B.S. 1400			
	Grade 9A	Grade 9B		Grade 9C		Grade 9D		AB1	AB2		—	
Copper, % . . . .	87.5	89		83 min.		81		87	80.25		89	
Aluminium, % . . .	9	10		10–11.5		11		10	9.75		11	
Iron, % . . . . .	3.5	1		3–5		4		3	5		5	
Nickel, % . . . . .	...	...		2.5 max.		4		...	5		5	
Manganese, % . . .	...	...		0.5 max.		...		...	...		...	
	As Cast	As Cast	Heat-Treated §	As Cast	Heat-Treated	As Cast	Heat-Treated ¶	As Cast	As Cast	Heat-Treated **	As Cast	As Cast
0.1% Permanent-Set Stress, † tons/in. <sup>2</sup>	...	...	...	...	...	...	...	10	17.0	26.4	22.6	...
Yield Strength, ‡ tons/in. <sup>2</sup>	12.0	14.3	17.9	15.7	23.2	20.1	31.3	...	...	...	...	...
Tensile Strength, tons/in. <sup>2</sup>	33.5	29.9	40.2	33.5	46.9	42.4	51.3	37.2	44.5	49.5	49.6	...
Elongation on 2 in., %	35	15	15	18	10	7	5	33	23	14	12	...
Brinell Hardness No.	120	140	180	155	230	195	235	129	170	229	212	...

\* *Materials and Methods*, 1954, 40, (6), 135.

† British Standard No. 18: "Tensile Testing of Metals". 1950: London (British Standards Institution).

‡ 0.5% extension; approximately equivalent to 0.15% permanent-set stress.

§ Water-quenched from 1625° F. (885° C.), tempered 1125° F. (610° C.), water-quenched.

|| " " " " 1625° F. (885° C.), " 1000° F. (540° C.), " " " "

¶ " " " " 1625° F. (885° C.), " 1150° F. (620° C.), " " " "

\*\* " " " " 1740° F. (950° C.), " 1110° F. (600° C.), air-cooled; not included in B.S. 1400.

The properties of the copper-aluminium-iron alloys can be considerably developed by heat-treatment, involving quenching from the  $\beta$  phase field followed by a low-temperature treatment; the complex aluminium bronzes respond to similar treatment. Examples are quoted in Table V.

#### IV.—ALLOYS USED IN PRACTICE

##### 1. COPPER-TIN ALLOYS

Of the copper-tin alloys used in industry, many are selected with particular regard to the suitability of their properties for service requirements, while others, such as the leaded gun-metals, have been developed because their founding characteristics are well adapted to making castings of the quality required.

The phosphor bronze PB 1, with tin not less than 10% and phosphorus not less than 0.5%, is used in particular for high-duty bearing applications, where high speeds and high loads are involved; hardened shafts should always be used with these bearings. Although a considerable quantity of sand castings is made in this alloy, it is prob-

ably most frequently supplied in the form of solid or cored sticks, and a number of plants are now coming into operation for the production of this alloy in the form of semi-continuously<sup>39</sup> or continuously<sup>40,41</sup> cast sticks and tubes. Another hard phosphor bronze, PB 2, is used principally for gears and has a higher tin content and lower phosphorus content, normally 12% tin and 0.3% phosphorus. These alloys depend for their strength and wear-resisting characteristics on a carefully controlled composition to give the desired structure, i.e. ( $\alpha + \delta + \text{Cu}_3\text{P}$ ) complex well distributed in a matrix of  $\alpha$  solid solution, the distribution being controlled by casting conditions.

When a softer alloy is required, one of the lead bronzes is used. These alloys usually contain from 8 to 25% lead, and are characterized by the presence of free lead particles distributed throughout their structure. The strength and wear-resistance of the matrix in which the lead particles are carried are imparted by additions of tin in various amounts to produce, in most alloys, ( $\alpha + \delta$ ) eutectoid in cored  $\alpha$ , although with additions of the order of 5% the eutectoid would not be formed. The alloys LB 1 and LB 2, with nominally 15 and 10% lead and 9 and 10% tin, respectively, are the strongest alloys in this group; while LB 4, with 10% lead and 5% tin, is suitable only for less onerous applications and is, of course, much cheaper. LB 5, with 22% lead and 5% tin, is an alloy of specialized application; it is necessary to control the lead and tin contents so as to avoid difficulties due to immiscibility in the liquid state (see p. 296). With all these alloys it is important to ensure a good distribution of the lead and ( $\alpha + \delta$ ) eutectoid. It is sometimes held that additions of nickel of about 1% are helpful in this connection, owing to the influence which nickel exerts on the solidification range of the alloy, but the author is not aware of evidence supporting this view.



The phosphor bronze PB 3 (10% tin, 0.3% phosphorus) and the lead-free gun-metals such as G 1 (88% copper, 10% tin, 2% zinc), known as "Admiralty Gun-metal", are employed for their strength and corrosion-resistance, particularly under marine conditions, and for the production of pressure-tight castings. These alloys are not so suitable for pressure-tight castings as the leaded gun-metals, but PB 3 is considered by some users to be superior to G 1 in this respect. For their strength these alloys depend upon the  $(\alpha + \delta)$  eutectoid in the micro-structure, with in the case of PB 3 a small amount of  $\text{Cu}_3\text{P}$  phase present in an  $\alpha$  solid-solution matrix. This

TABLE VI.—*The Influence of Gas Content on the Quality of Gun-Metals and Phosphor Bronzes.* (Mantle.<sup>44</sup>)

Alloy	Casting Temp., °C.	U.T.S. of D.T.D. Bar, tons/in. <sup>2</sup>	U.T.S. of Strip Cut from Casting, tons/in. <sup>2</sup>	Pressure-Tight Castings after Machining, %
<b>A. Castings Made from Gas-Free Metal</b>				
85 : 5 : 5 : 5 leaded gun-metal (B.S. 1400, LG2)	1180	15.5	10.5	90
86 : 7 : 5 : 2 leaded gun-metal (B.S. 1400, LG3)	1180	17.5	9.5	80
88 : 8 : 4 gun-metal* (B.S. 1400, G2)	1180	20	7	Nil
90 : 10 phosphor-bronze with less than 0.25% phosphorus (B.S. 1400, PB3)	1130	19	... §	Nil
90 : 10 phosphor-bronze with 0.5% phosphorus (B.S. 1400, PB1)	1130	18	... §	100
<b>B. Castings Made from Slightly Gassy Metal †</b>				
85 : 5 : 5 : 5 leaded gun-metal	1180	13	9.5	85
86 : 7 : 5 : 2 leaded gun-metal	1180	15.5	9.5	50
88 : 8 : 4 and 88 : 10 : 2 gun-metal	1180	17.5	10.5	75
90 : 10 phosphor-bronze, 0.2% P	1130	16	... §	25
<b>C. Castings Made from Moderately Gassy Metal ‡</b>				
85 : 5 : 5 : 5 leaded gun-metal	1180	11	8.5	55
86 : 7 : 5 : 2 leaded gun-metal	1180	11.5	8.5	15
88 : 8 : 4 and 88 : 10 : 2 gun-metal	1180	13	8.5	25
90 : 10 phosphor-bronze, 0.2% P	1130	13	... §	Nil

\* Similar results were obtained for 88 : 10 : 2 Admiralty gun-metal (B.S. 1400, G1).

† Metal has picked up sufficient gas during melting to produce 2% voids in the test-bars for each alloy.

‡ Metal has picked up sufficient gas during melting to produce 3.5% voids in the test-bars for each alloy.

§ Not determined.

type of structure provides in addition a measure of wear-resistance, so that the alloys can also be used for less onerous bearing applications. It is particularly necessary to ensure the maximum possible density, with residual porosity well distributed, especially for pressure-tight castings.

While the lead-free gun-metals have superior strength and corrosion-resistance compared with the leaded gun-metals, the latter are superior for the production of pressure-tight castings.<sup>42, 43</sup> A paper of particular interest by Mantle<sup>44</sup> compares the leaded and lead-free gun-metals and phosphor bronzes, and quotes values

which are reproduced in Table VI. LG 3 (87 : 7 : 4 : 2) has  $(\alpha + \delta)$  eutectoid in the structure with some lead phase also present, while LG 2 (85 : 5 : 5 : 5) contains little, if any,  $(\alpha + \delta)$  eutectoid but rather more lead phase. These structures impart reasonable bearing properties for low-duty applications, and the alloys are also used for backing-castings for white-metal-lined bearings; probably their main application, however, is for pressure-tight castings, including steam valves. They depend for their popularity on the relative facility with which pressure-tight castings can be made in them. In production, the important factors are to maintain the composition within the required limits, but above all to control the amount, form, and distribution of porosity.

Attention is drawn to papers by Hudson,<sup>43</sup> Vanick,<sup>45</sup> and the International Nickel Company<sup>46</sup> on the influence of nickel on these alloys, although nickel additions are not necessary for the production of pressure-tight castings. Work reported by Pfeil<sup>47</sup> indicates that nickel additions have a beneficial influence in offsetting the adverse effect of heavy sections on the actual mechanical properties of the casting. With a tin content of not less than 4%, as nickel additions are increased above 3% the alloy becomes more responsive to heat-treatment; papers by Vanick<sup>48, 49</sup> refer to the heat-treatable nickel-tin bronzes. The influence of nickel as a grain refiner has been studied by Colton and Margolis.<sup>50</sup>

## 2. COPPER-ZINC ALLOYS

The simple  $\alpha$  brasses are low-strength alloys used for general plumbing fittings and other applications in which there are no onerous conditions requiring strength or corrosion-resistance. The sand-cast alloys, SCB 2 and 3, contain lead to facilitate machining, and SCB 1 in addition contains tin to impart corrosion-resistance. Naval brass (SCB 4) is nominally 60 : 40 brass, an  $\alpha/\beta$  alloy of higher strength; it contains 1% tin for corrosion-resistance, particularly against marine conditions. The tin also to some extent improves the mechanical properties. The die-cast alloys are also  $\alpha/\beta$  alloys based on 60 : 40 brass, containing tin (Naval brass, DCB 2) or tin-free (DCB 1). Impurities, particularly lead, are rigorously excluded, but aluminium is added to improve fluidity. Die-castings can, however, be made in a free-machining lead-containing brass<sup>38</sup> (DCB 3) provided that the design is suitable, with economy in cost of metal and machining.

The silicon-containing brasses of suitable composition have attractive mechanical properties and have found wide application for pressure die-castings in America; incidentally, they have been used in the U.S.S.R. to replace tin bronzes.<sup>51</sup> With suitable techniques these alloys can be gravity die-cast, and it is surprising that they are not more used in Britain, especially as they can be cast at very much lower temperatures than the ordinary brasses.

The high-tensile brasses are essentially specialist alloys, and have been developed to give specific properties or combinations of properties, which include high strength and resistance to corrosion and to corrosion-fatigue. Most manufacturers work to their own specifications, which have to be of very much closer limits of composition than those of B.S. Schedule 1400.

High-tensile brasses were originally developed during

the latter part of the last century, the first patent, due to Parsons,<sup>52</sup> being taken out in 1876. They were developed for their combination of strength and corrosion-resistance, particularly under marine conditions, and alloys with this combination of properties today form the majority of the high-tensile brasses used in practice. They are of  $\alpha/\beta$  microstructure, possess tensile strength between 30 and 38 tons/in.<sup>2</sup>, and can have a high resistance to fatigue. The compositions normally fall within the broad specification limits of HTB 1, but minimum values specified by individual manufacturers or users for the tensile strength vary from 30 to 34 tons/in.<sup>2</sup>, proof stress from 11 to 16 tons/in.<sup>2</sup>, and elongation values not less than 20%. Compositions, based upon the considerations of the preceding section, are selected to combine strength and corrosion-resistance.

Alloys of higher strength, such as HTB 2, should always have an  $\alpha/\beta$  structure; they generally contain about 5% aluminium and are tin-free. Tensile strengths specified vary from 38 to 44 tons/in.<sup>2</sup>, proof stresses from 18 to 22 tons/in.<sup>2</sup>, and elongation values from 15 to 20%.

The very strong high-tensile brasses (HTB 3), with tensile strength of the order of 50 tons/in.<sup>2</sup>, proof stress of the order of 30 tons/in.<sup>2</sup>, and elongation 18%, are always all- $\beta$  alloys, chosen for their high strength, but must be used with caution because of their susceptibility to stress-corrosion cracking. They invariably contain about 5% aluminium.

### 3. COPPER-ALUMINIUM ALLOYS

These, like the high-tensile brasses, are specialist alloys; only two are included in B.S. Schedule 1400. The alloy AB 1 is a simple  $\alpha/\beta$  alloy of lower strength, containing copper, aluminium, and iron, used for sand casting or die-casting. AB 2 is a high-strength, complex aluminium bronze based on the composition aluminium 10, iron 5, nickel 5%, remainder copper, although various companies which specialize in the manufacture of this alloy have an individual preference in the precise composition which they adopt, particularly with regard to the aluminium content.

Some manufacturers of the complex alloys favour the inclusion of manganese, which increases the solidification range and modifies the nature of the oxide film formed on the molten metal with consequent effects upon the casting characteristics; effects which are evidently believed to constitute an improvement, although in the author's experience they afford no advantage.

In America the copper-aluminium-iron alloys are preferred,<sup>53, 54</sup> used in the heat-treated condition, if properties superior to those of the as-cast alloys are required (Table V, p. 302). Apart from the problems introduced by the quenching of complex or large castings, the overall properties of the complex nickel-containing alloys used for higher strength in Britain are considered more suitable for most applications for which such alloys are normally selected.

## V.—THE INFLUENCE OF IMPURITIES (OTHER THAN REDUCING GASES)

### 1. COPPER-TIN ALLOYS

As reducing gases are of exceptional importance, particularly in the case of the copper-tin alloys, a separate section is devoted to them. Discussion of the effect of

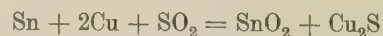
oxygen cannot, however, be completely divorced from a consideration of the effect of water vapour and hydrogen, since oxides are formed in the reversible "steam-reaction". According to this reaction, vapour is dissociated by copper or bronze to form oxygen and hydrogen, which co-exist in the molten alloy and recombine during solidification according to the equation normally given as:



In the reactions of copper-tin alloys with oxygen, copper oxide ( $\text{Cu}_2\text{O}$ ) is reduced by tin to  $\text{SnO}_2$ , while in the presence of zinc a mixture of the oxides  $\text{SnO}_2$  and  $\text{ZnO}$  is formed. These oxides are important impurities which do not readily separate from the melt, and as they reduce fluidity and inhibit feeding, they lead to unsoundness. With the addition of phosphorus, fluid phosphates are formed which separate to the surface of the metal. A study of the reactions which take place between oxygen and water vapour, as well as other gases, and alloys of copper and tin, based on the principles of thermodynamics, was published by Lepp<sup>55</sup> in 1949.

Aluminium and silicon form oxides which phosphorus will not reduce and which seriously inhibit feeding; small amounts of these elements, of the order of 0.005–0.01%, are harmful, but analytical methods suitable for routine production use are not sufficiently accurate for control to the required limits. In alloys containing lead, the influence of silicon is reported as being more marked because of the formation of a flocculent lead silicate which seriously affects fluidity and inhibits feeding. Manganese is another element in this oxide-forming group, objectionable but less dangerous than aluminium or silicon; in alloys containing lead, it does not prove so harmful, in that a fluid slag is formed.

Sulphur can be introduced as an impurity in the metals melted or by the reaction of sulphur dioxide in the furnace atmosphere with molten bronze, and leads to the formation of sulphides. In the case of the alloys of copper and tin alone, it would appear that the sulphides of both elements are formed and reduce fluidity and inhibit feeding in the same way as oxides. It is not clear what happens in the presence of zinc, but in the leaded alloys sulphide particles are usually found associated with the lead constituent. It is also reported that the reaction:



is reversible under certain conditions, particularly when high temperatures are involved.<sup>56</sup> There is, however, a marked lack of information concerning the influence of sulphur on these alloys, and research is in hand on the subject at the B.N.F.M.R.A. This is of particular importance currently because of the economic advantage to be derived from the use of heavy fuel oils, which have a high sulphur content. Lepp<sup>55</sup> states that in the alloys of copper and tin the sulphides  $\text{Cu}_2\text{S}$  and  $\text{SnS}$  are formed; he is categorical that the presence of sulphur is significant and that the problem of desulphurization of copper-tin is important. Sulphur has been added to the lead bronzes, on the grounds that it assists in achieving a fine distribution of lead;<sup>57</sup> Guertler and Landau have shown that it extends miscibility in copper-lead alloys.<sup>58</sup>

Iron has an adverse effect on metal fluidity in amounts exceeding 0.1 or 0.15%, and its effect on the surface



film of fluid phosphates can immediately be recognized. The presence of iron in these amounts also leads to the presence of an iron-rich phase in gun-metals, while in phosphor bronze an iron-tin compound is formed with serious embrittling effects.

Zinc as an impurity in copper-tin alloys (as discussed while considering it as an alloying element) will increase the amount of the ( $\alpha + \delta$ ) eutectoid present, apart from its effect in forming oxides. In the chill-cast alloy zinc has an adverse effect unless sufficient phosphorus is present to ensure reduction of zinc oxide; in phosphor bronzes of higher phosphorus content, however, it is claimed that up to 0.25% zinc might be beneficial on account of its effect in reducing the level of the residual oxygen content. Other elements which go into solution to increase the proportion of the ( $\alpha + \delta$ ) eutectoid are arsenic, antimony, and aluminium, and in small amounts iron, phosphorus, and nickel.

According to work carried out many years ago on sand-cast gun-metals, antimony increases the amount of the eutectoid, but is relatively harmless in small amounts up to probably 0.4%.<sup>59, 60</sup> Larger amounts were reported to result in increased porosity and a reduction in properties in sand-cast alloys, although in chill-cast alloys they could be tolerated. Work by Hanson and Pell-Walpole<sup>6</sup> shows, however, that in chill-cast phosphor bronze and low-tin leaded bronze only a slight adverse effect is produced by additions up to 1%. In high-tin bronze and gun-metals an appreciable deleterious effect is experienced with 0.2%, and Hanson and Pell-Walpole recommend maximum limits of 0.5 and 0.05% for these groups, respectively. In view of the earlier work, it would be interesting to know the effect of antimony on the sand-cast alloys, particularly as it is a common impurity arising from the contamination of swarf with white metal. The effect of arsenic, frequently introduced by the use of arsenical copper, is not serious in amounts which might normally occur, say, up to 0.2 or 0.3%.

Phosphorus as a deoxidizer in copper-tin alloys or the gun-metals is added in deliberate excess, and if this excess is above 0.2 or 0.02% for these alloys, respectively, it may promote metal/mould reaction which increases gas unsoundness, although in certain circumstances this effect can be used beneficially. Excess phosphorus beyond the solubility limit will form  $\text{Cu}_3\text{P}$ , as has already been described. If present in sufficiently high amounts, it can lead to mould penetration and scabbing.

Impurities which can remain in elemental form to exercise a deleterious effect are bismuth and lead. Bismuth, in lead-free alloys, forms intercrystalline films which are embrittling, but with lead present bismuth forms a eutectic and its deleterious effect is avoided. Lead as an impurity is not so deleterious as bismuth, in that it is distributed throughout the structure in globular form and in small amounts has only a slightly harmful effect on strength and ductility.

For further information original work or reviews of this subject may be consulted.<sup>6, 61, 62</sup>

## 2. COPPER-ZINC ALLOYS

An essential feature of the commercial sand-cast brasses is that wide limits are permissible as regards impurities and that they are cheap. It is important that impurities should not be allowed to impair the economic production

of satisfactory pressure-tight castings. For example, aluminium tends to form oxide films which may become entrapped unless special precautions are taken in casting to exclude them; while the presence of iron much in excess of the solubility limit may affect the surface finish of subsequent electrodeposited coatings.

In the case of the die-cast brasses, impurities which would affect hot shortness, such as lead and bismuth, are rigorously excluded and virgin metals are normally used. More recently, with appropriate techniques and where the designs of the components to be cast are suitable, leaded alloys have been employed for their free-machining qualities.<sup>38</sup> Aluminium is introduced to improve fluidity and to provide a good surface finish, the entrapment of oxide films being avoided by the adoption of a suitable foundry technique. Impurities do not exercise an adverse effect on the soundness of castings in high-tensile brasses, provided that the proper precautions are taken to avoid oxide-film entrapment, but they affect strength and ductility owing to their purely metallurgical effects. With increase in the proportion of the  $\beta$  phase, the deleterious effects become more marked. It has already been indicated that it is undesirable that tin and aluminium should be used together in quantities beyond certain limits; for example, tin should not exceed 0.25% in an alloy containing 5% aluminium, nor should aluminium be allowed to exceed 0.3% in an alloy containing more than 1.2% tin. Such undesirable combinations might arise from lack of control over composition or from contamination.

While lead can have beneficial effects on the machining characteristics of high-tensile brasses, it has an adverse effect on strength and ductility, and antimony and bismuth in quite small proportions also seriously affect these properties; in die-casting alloys, these elements would seriously promote hot shortness. While some alloys include nickel as an essential element,<sup>63</sup> in many of the alloys of those compositions most commonly used it would have a harmful effect, particularly if present in excess of 1%.

Silicon does not form separate constituents, but has an adverse effect on the properties of the alloy and has a high zinc equivalent. It is capable of forming silicates, which can lead to a significant loss of iron from the alloy. Silicates can also be introduced from the furnace lining or in fluxes, with similar effect. It is interesting to note that the presence of silicon can be detected in amounts as small as 0.05%, by the fact that it inhibits the darkening of the iron-rich constituent on etching with acid ferric chloride, owing to the formation of acid-resisting silicon-iron. Silicon also influences the appearance of the  $\alpha$  phase, increasing the angularity of the particles. Silicon can be picked up from siliceous fluxes, acid furnace linings, or from crucibles containing considerable amounts of silicon carbide. Excessive contamination with silicon has been associated with the formation of hard spots which cause difficulty during machining.

## 3. COPPER-ALUMINIUM ALLOYS

In view of the applications for which these alloys are employed, and the fact that their suitability has been established using alloys made from high-grade virgin materials, it is considered most unwise that metal other than that of the highest quality should be used.



Lead has only a slight effect on the mechanical properties in additions up to 1%, and considerably facilitates machining. Its influence on other properties, such as fatigue and corrosion-resistance, has, however, not been investigated. It seriously affects the hot shortness of the alloy and, even in small quantities, the welding characteristics. Small amounts of tin, silicon, and magnesium have a seriously adverse effect on the mechanical properties. Probably the element which has the least harmful effect on the mechanical properties is zinc, and its presence is normally permitted up to 0.5%.

While contamination by other metals is the most probable source of impurities, silicon can be picked up from crucibles, furnace linings, or fluxes, and precautions should be taken to avoid this.

## VI.—THE INFLUENCE OF REDUCING GASES

### 1. COPPER-TIN ALLOYS

The evolution of gas during solidification is probably the most significant factor influencing the quality of castings in alloys based on copper-tin. An exhaustive literature on the occurrence of porosity in, and the influence of gases on, copper and copper-tin alloys, has been reviewed by Pearson and Baker,<sup>64</sup> and by Pell-Walpole.<sup>65</sup> While it is difficult to select the most important contributions, stages in development may be mentioned. Before 1930 porosity was largely attributed to shrinkage or oxidation. In 1930 and 1933 Allen<sup>66, 67</sup> and his colleagues published their work on the "steam reaction" in connection with copper, to which reference has already been made. In 1930 a paper was published by Daniels<sup>68</sup> discussing the influence of gases on bronzes, including reference to the "steam reaction", and this was followed by Lepp's<sup>69</sup> work on the bronzes. In 1934 Lepp took out patents<sup>70</sup> covering a process for the preparation of copper-tin alloys employing an oxidation technique. The fluxes used included alkali carbonates to serve as carriers for the oxide, but probably also for the removal of sulphur. These fluxes severely attacked Salamander crucibles, and alternative oxidizing fluxes were suggested by other workers. Pell-Walpole<sup>65</sup> reported in 1944 the development of a flux-degassing process for chill-cast tin bronzes, using a flux containing borax, sand, and cupric oxide. While methods involving melting under oxidizing conditions might be more accurately regarded as preventive than as degassing techniques, scavenging methods in which inert gases were passed through the metal were also considered.

In 1936 Baker and his colleagues at the B.N.F.M.R.A. began their attempt to clarify the unsatisfactory position which existed because of the lack of a clear understanding of the causes of unsoundness in bronze castings. This they did by a most careful and systematic study of the influence of shrinkage and dissolved gases on the soundness and properties of bronze castings. As this work has an important bearing on methods now used for the control of casting quality and brings out the important points concerning the influence of gases, a brief review of it is given.

In the first paper,<sup>64</sup> published in 1941, attention is drawn to the fact that, owing to the long freezing ranges of the copper-tin alloys, they are prone to shrinkage unsoundness in the form of interdendritic fissures, and that no distinction can be observed between cavities due

to shrinkage and those due to gas evolution. While gas unsoundness can result from the evolution of carbon monoxide, hydrogen, water vapour, or sulphur dioxide during solidification, hydrogen and water vapour are likely to prove the most harmful; carbon dioxide and nitrogen are insoluble and therefore without adverse effect. Small amounts of hydrogen may have a beneficial effect on chill-cast bronzes, but they have a serious effect on sand castings (a point subsequently qualified), while larger amounts of hydrogen lead to gross unsoundness, which can be of spherical form. In discussing the reversible "steam reaction", it is pointed out that in alloys containing phosphorus, solubility of oxygen would be very low and unsoundness would be due to hydrogen; while in alloys which do not contain phosphorus steam unsoundness can be avoided, either by deoxidation, or by oxidation to remove the hydrogen: the soundness of the principle of melting under oxidizing conditions for the elimination of reducing gases such as hydrogen, is verified.

In the first of two papers<sup>71</sup> published in 1944, the beneficial effect of oxidizing fluxes is confirmed, but both zinc and phosphorus are reported to hinder the removal of hydrogen by oxidation. In further work degassing was effected by scavenging, either by charging manganese ore to the bottom of the crucible before melting, or by the use of nitrogen after melting; both methods gave castings of high density and excellent mechanical properties. In the second paper<sup>42</sup> it is recorded that a small amount of gas dissolved in the metal serves to disperse the porosity more uniformly, thereby obviating harmful concentrations of porosity in those parts of the casting in which solidification is delayed. It is also shown that the leaded gun-metals are more suitable for difficult pressure-tight castings<sup>43, 44</sup> than those which are lead-free, and methods for melting the various copper-tin alloys are recommended.

Subsequent papers by Glaisher<sup>72</sup> and by Rutherford,<sup>73</sup> in 1949 and 1951 respectively, indicate that a controlled amount of gas pick-up in the mould is advantageous in preventing the occurrence of harmful concentrations of porosity in castings; to effect this the metal/mould reaction is promoted by leaving a deliberate excess of phosphorus in the metal as it is poured. Details are given of the effect on metal/mould reaction of impurities in the metal, of mould material, of additions to the sand, and of mould dressings, including reference to a dressing in the form of aluminium-magnesium paint for preventing metal/mould reaction from taking place. The importance of the relationship between section thickness and casting temperature is emphasized.

The last paper to appear concerning the B.N.F.M.R.A. work, that by Rutherford<sup>74</sup> in 1952, which reports further experimental results and rounds off the results of the earlier work, is probably the most useful as far as practice is concerned. It is recognized that the advantages of metal/mould reaction are more marked for the phosphor bronzes and the lead-free gun-metals than for the leaded gun-metals. The paper includes references to work by Mantle,<sup>75</sup> to which reference is also made elsewhere, concerning the practical application of the technique involving nitrogen degassing followed by metal/mould reaction, in a production foundry making valve bodies; as a result the amount of scrap due to leakage on pressure test was significantly reduced.



The application of the results of this research in practice are considered later in the present paper when the relative usefulness of metal/mould reaction in connection with various alloys is discussed.

## 2. COPPER-ZINC ALLOYS

It was thought for many years that hydrogen was insoluble in brasses in significant amounts owing to the high vapour pressure of zinc. It has, however, been shown by the author that inverse segregation can occur in large castings which solidify slowly in these alloys (see Section IX, p. 312), and that the presence of dissolved gas can be a significant factor. Gas contents of the order of 0.5 c.c./100 g. at N.T.P. can prove critical. Alloys of high tin content, of the order of 1%, are more susceptible to the influence of gas than others.

Gas pick-up can be greatly influenced by the use of certain types of fluxes during melting, particularly in open-flame furnaces.

## 3. COPPER-ALUMINIUM ALLOYS

If normal care is exercised during melting, and excessive heating and stewing are avoided, the aluminium oxide film on the surface of the metal serves to prevent gas pick-up in the absence of any flux or other cover.<sup>81</sup> If, however, fluxes are used which dissolve the oxide film, or if the metal is excessively heated, hydrogen can readily be dissolved. When melts are badly gassed, the excessive dissolved gas comes out of solution during solidification, producing a characteristic type of porosity, sometimes spherical, but frequently in the form of "worm holes". A paper has been written by Schwietzke on the influence of hydrogen and water vapour on aluminium bronze.<sup>76</sup>

# VII.—THE CONTROL OF METAL QUALITY: ALLOYING AND METAL PRACTICE

## 1. COPPER-TIN ALLOYS

### (a) Foundry Practice

Up to the early 1930s, the copper-tin alloys were melted under charcoal or neutral fluxes based upon borax or glass, to prevent oxidation of the metal. In all foundries the fluidity of the phosphor bronzes was well known. Although it was probably not widely appreciated that phosphorus removed harmful oxides by forming fluid phosphates, or that a small amount of phosphorus was necessary to prevent increase in oxygen content during pouring, a small addition of phosphorus was made to the other alloys of the group just before casting "to improve the fluidity of the metal".

During the decade which followed, with increase in knowledge on the influence of gases, with the development of melting techniques to prevent gas pick-up during melting, and with the introduction of degassing by scavenging, many foundrymen changed their methods. In 1932 oxidizing fluxes became available from foundry suppliers for use by plunging, and by 1938 similar fluxes were in use as covers during melting. Gun-metal ingots were melted under oxidizing conditions in some foundries, while in others manganese ore was charged to the bottom of the crucible. These techniques, however, had an economic effect on crucible life, since certain oxidizing fluxes attacked the crucible at the metal line,

while manganese ore penetrated the crucible at the bottom by chemical reaction. A further important factor was the difficulty in controlling metal composition when melting ingots or scrap under oxidizing conditions, owing to the preferential oxidation of the constituent elements. The method also involved such economic factors as increased melting losses and the cost of the fluxes employed.

An important development, introduced into practice after 1945, is the use of scavenging methods for degassing after melting. The plunging of marble chips has been shown to be effective, and currently the use of calcium cyanamide in a similar way is being attempted. Nitrogen degassing is widely used but the cost of nitrogen and of the rather fragile graphite or plumbago tubes has to be taken into account. In foundries where it is possible to install permanent degassing apparatus near the furnaces, or where degassing stations can be set up, the fragility of the equipment is of less importance and a regular routine can be satisfactorily developed; but in jobbing foundries, where the equipment must be flexible and mobile, the process is not convenient and it is not easy to establish satisfactory conditions. Degassing with nitrogen in normal crucible melts up to 1000 lb. can be effected by bubbling the gas through the melt for 5-7 min. at the fastest rate possible without causing excessive splashing; it has been recommended that the gas pressure in the cylinder should not be allowed to drop below 20 atm. to prevent moisture passing from the cylinder, but some doubt has been thrown on the necessity for this by recent work which has still to be confirmed. The availability of these scavenging techniques provides an alternative to the use of oxidizing fluxes as covers during the melting of ingots: charcoal covers can be substituted and, if necessary, the melt can be degassed by scavenging with nitrogen. The use of charcoal results in reduction in metal losses during melting and facilitates control of composition: if degassing is necessary, metal losses will be incurred during the superheating necessary before degassing and during the degassing operation itself, but on balance it is probable that saving will result. Vacuum degassing has not been widely applied in production, but a paper has been published comparing results obtained with the effectiveness of lateral taper chills.<sup>77</sup>

If virgin metals are used, with the correct melting and alloying technique there is no reason why castings should not be poured directly, without pre-ingotting. It is normal foundry practice either to include a constant proportion of runners and risers in virgin heats, or to melt these separately in heats consisting entirely of runners and risers. Appropriate allowances must be made for losses during melting, and variations in practice are necessary according to whether a virgin melt is made, or runners and risers are being re-run: for consistency and ease of operation in the foundry it is preferable to maintain a constant proportion of runners and risers in each heat. Of the copper-tin alloys in normal production, virgin metals are probably employed only for those used under more onerous conditions, such as high-duty bearings (PB 1), gear wheels (PB 2), and for the higher-class lead-free gun-metal (G 1), or phosphor bronze (PB 3), pressure-tight castings. These alloys can, of course, be obtained as secondary ingots, but because of the relatively high degree of purity required there would prob-



ably be only a slight advantage in price, as compared with using virgin metal. While cost is an important factor, there must be offset against any possible saving the possibly greater variations in composition and the introduction of impurities if secondary materials are used. There is a considerable lack of knowledge of the effects of impurities on the service properties of alloys such as PB 1, PB 2, and G 1, and many users and suppliers rightly prefer not to take risks with alloys used for high-grade applications.

The vast majority of castings in the lower-grade alloys, such as the leaded gun-metals, are, for economic reasons, made from secondary ingots, and this opens up a wide source of possible contamination—a matter vital to the control of quality. For this reason there is an urgent need to learn more of the effect of impurities on casting characteristics and properties of the sand-cast alloys. Another source of contamination to which attention can conveniently be drawn at this point is the mixing of foundry returns to metal stores owing to carelessness or absence of identification. This is a serious problem affecting equally all alloys, particularly in jobbing foundries handling various types of material, and careful attention should therefore be devoted to foundry organization in this respect. It is good practice, when using secondary ingots, to incorporate a proportion of runners, risers, and scrap castings with each charge, so that consistency in the composition of the product can be maintained.

Both to control the gas content of the metal and to maintain consistency in composition, it is necessary to melt these alloys as rapidly as possible, and for the foundry to be so organized that when the metal is ready at the required temperature for pouring, the mould should be ready, the crane available, and all other details in order so that the metal can be cast. All tools should be properly maintained and well preheated before use.

The choice of furnace equipment,<sup>78</sup> the condition in which it is maintained, and the fuel used<sup>79</sup> can influence the quality of these alloys, in as much as rate of melting and atmosphere control are affected. Probably the greater proportion of metal for casting is melted in oil-fired crucible furnaces, and although choice of crucible is not particularly important, some types enable melting to be effected more rapidly than others. If coke is used, this should be kept dry. If furnaces are employed in which the flame comes into contact with the metal, the question of the effect of the flux both on the metal and on the furnace lining assumes importance. Flame control in these furnaces is also important because of the effect of atmosphere on metal composition and dissolved gas content. A further factor is the possible influence of the sulphur content of the fuel, which in the case of coal or heavy fuel oil may be high: as mentioned in the section on impurities, the effect of sulphur picked up by the metal from the furnace gases is not properly understood. As most secondary ingots are made in furnaces of this type, sulphur is frequently present as an impurity, sometimes in considerable quantities.

#### (b) *Melting Practice*

Normal melting practices for these alloys will now be outlined; where alternatives are quoted, it is desirable that whichever procedure is adopted should be used consistently.

#### (i) *Phosphor Bronzes*

If the alloy is to be made from virgin metal, the copper is melted with a slightly oxidizing furnace atmosphere, using either charcoal or an oxidizing flux cover. The cover is skimmed off before adding part of the phosphorus addition as phosphor copper, allowing 0.05% phosphorus for deoxidation; this is followed by the tin addition and finally by the remainder of the phosphor copper. Ingot metal or scrap is melted under slightly oxidizing conditions, using a neutral flux cover or charcoal.

It is usually desirable to degas the metal by passing a rapid stream of either air or nitrogen through the melt; alternatively, proprietary scavenging materials which are plunged can be used. If air is used this is taken from cylinders containing air at not less than 20 atm. pressure to avoid the necessity of using drying equipment; the normal foundry air supply is not suitable. The phosphorus contents required by the phosphor bronze specifications are sufficient to promote metal/mould reaction, unless an inhibiting paint is used on the moulds. With thin sections (about  $\frac{1}{8}$  in. or less) benefit is likely to be derived from metal/mould reaction, but with heavier sections it is advisable to minimize the effect of gases from the reaction by pouring at low temperatures or by the use of an inhibiting mould dressing.

#### (ii) *Lead Bronzes*

The virgin metal is made in accordance with the first method given below for the leaded gun-metals, and the same considerations apply to melting ingots and scrap as for the leaded gun-metals. Some authorities consider it preferable to pre-ingot those alloys with more than 10% lead content, in order to secure a satisfactory distribution of lead, but in the author's experience this is not necessary. Excess phosphorus can lead to metal/mould reaction, as in the other copper-tin alloys; the precise amount is dependent upon composition, but it is higher than in the case of the zinc-containing alloys.

#### (iii) *Lead-Free and Leaded Gun-Metals*

With virgin metals the copper is melted with a slightly oxidizing furnace atmosphere, using either an oxidizing flux or a charcoal cover which is skimmed off before adding 0.05% phosphorus for deoxidation; this is followed by the zinc and tin, and lead (if any), and a final addition of phosphorus. Alternatively, the first phosphorus addition is omitted, and an addition of 0.25% zinc allowed over and above the alloying requirement, for loss in deoxidation. In either case the amount of the phosphorus addition is so adjusted that the residual amount is related to whether or not metal/mould reaction is desired. Ingot metal or scrap is melted under slightly oxidizing conditions, using either an oxidizing flux or a charcoal cover.

If the metal is to be degassed, nitrogen is normally used and the operation is carried out before making the final addition of phosphorus. If it is desired to promote metal/mould reaction (which is likely to be beneficial only with castings of light section (about  $\frac{1}{8}$  in. or less) unless low casting temperatures can be used) the final phosphorus addition has to be sufficient to provide for deoxidation and to leave a residual content of 0.06–0.08%, in total about 0.10%. With castings of heavier



section, if low casting temperatures cannot be used, residual phosphorus is maintained at about 0.02%.

Gun-metal ingots melted under slightly oxidizing conditions in oil-fired crucible furnaces, using a charcoal cover, are not so easily excessively gassed as is sometimes imagined, provided that melting is reasonably rapid and the metal is not stewed. With the leaded alloys the residual gas content is suitable for the manufacture of pressure-tight castings without degassing and without promoting metal/mould reaction: a final phosphorus addition of 0.04% is suitable. While this practice can also be used for the lead-free alloys, the technique previously described is likely to prove more trouble-free. The French foundry industry also recommends the use of charcoal covers with leaded gun-metal.<sup>80</sup>

Finally, it should be emphasized that care must be taken to ensure that the metal poured contains not less than about 0.02% phosphorus; with less than this amount present there is a danger that the oxygen content will be increased sufficiently during pouring for the "steam reaction" to occur and cause porosity in the castings.

## 2. COPPER-ZINC ALLOYS

The sand-cast brasses are normally purchased by the foundryman as ingots, while the die-cast brasses are either similarly purchased or made from virgin metal or selected wrought-brass scrap.

The essential features in making high-tensile brass are, first, to make certain that the iron constituent is properly alloyed, and secondly, to ensure adequate mixing. The normal procedure is to charge the iron and copper, which is heated to above 1300° C. and thoroughly mixed to make sure that the iron is properly dissolved. Manganese can be added, either as ferro-manganese with the initial charge, or as manganese copper at this stage. This is followed by the addition of aluminium, tin, and lead, if any, and finally by the zinc. The metal is then again thoroughly mixed and normally poured into ingots.

It would not generally be convenient or economic to carry out the operation of alloying high-tensile brass for the direct pouring of castings. It is also desirable and easier to make the metal in large heats, e.g. in 1000-lb. crucible furnaces, whereas the amounts required for castings might vary considerably. Provided that the metal is properly alloyed and free from gas, however, there is no metallurgical advantage in pre-ingotting, apart from a possible improvement in the dispersion of the iron-rich phase during remelting.

An essential consideration is to control the zinc content of the metal during melting, and to adjust it if necessary before casting. Fluxes are not needed in melting these alloys if reasonable care is taken to avoid overheating, and in crucible melting, melting losses are not normally high. When the metal is melted in open-flame furnaces, however, losses are likely to be greater but can be reduced by the use of suitable fluxes. If large castings are to be made which have slow cooling rates, gas pick-up, due to the use of fluxes, may be excessive and can lead to casting defects (see Section IX, p. 312). When using open-flame furnaces, it is necessary to guard against the effect of siliceous slags, arising from the excessive heating of acid bricks or attributable to the fluxes, which can lead to a marked reduction in the iron

content of the metal and the pick-up of silicon as an impurity.

It is, of course, normal to charge runners and risers in a reasonable proportion with virgin ingots.

It has already been stated that these are specialist alloys from the point of view of the selection of suitable alloys for service requirements, and they are equally specialist alloys in relation to their preparation. The greatest care must be taken in the manufacture of secondary ingots from miscellaneous scrap. It would be a matter of extreme difficulty to increase the iron content of the alloy and to reproduce the iron-rich phase in its correct form. The introduction of coarse particles of free, iron-rich material can cause rusting under corroding conditions and lead to difficulties in machining. Moreover, only properly alloyed iron is effective for its purpose.

## 3. COPPER-ALUMINIUM ALLOYS

As in the case of the high-tensile brasses, it is first necessary to ensure that the iron and nickel (if any) which are charged with the copper are properly alloyed; an unreasonable copper loss can lead to a significant variation in aluminium content. The aluminium is then added, and it is at this stage that the greatest care has to be taken to ensure complete mixing. While it is economically desirable to use rapid-melting crucibles, and with normal practice these are quite satisfactory, it is well to bear in mind that silicon can be picked up from the silicon carbide normally used in their manufacture. For the same reasons as are given under "High-Tensile Brass", it is normal to pour ingots, which are subsequently remelted as required, for the production of castings.

If the metal is remelted in crucibles, it is advisable not to use fluxes<sup>81</sup> and to avoid excessive heating and stewing in order to prevent gas pick-up and to minimize loss of aluminium. If the metal is melted in open-flame furnaces, the possibility of picking up gas is considerably increased; again this depends upon whether or not fluxes are used and the care taken in the melting procedure. It is wise to take precautions against silicon pick-up by care in choice of flux, and in all cases to avoid excessive temperatures. It is possible to make large castings using reverberatory furnaces without excessive gas pick-up; if an undue amount of gas is dissolved it can be removed by nitrogen degassing.

"Hardeners" are frequently used in the manufacture of copper-base alloys, and a paper by Voce<sup>82</sup> includes compositions, melting points, and reasons for their use.

## VIII.—TESTS FOR METAL QUALITY

The metal at the time of pouring must be suitable for the production of castings of the desired standard, and tests are required for quality-control purposes. A specification is necessary to cover both acceptance tests for virgin or secondary ingots, if these are purchased, and acceptance tests for the metal used for the castings.

The preparation of specifications presents considerable difficulty with the copper-tin alloys, but less difficulty with the high-tensile brasses and aluminium bronzes. Basic composition, permissible impurity levels, and mechanical tests are normally specified. Wet methods

for chemical analysis are well established, and spectrographic techniques have been devised, and are extensively used by the limited number of firms who have the equipment, although they are not yet entirely satisfactory in all cases. Physico-chemical methods have also been described for some determinations; the B.N.F.M.R.A. have in hand a research on methods for chemical analysis. It is pertinent to recall that test-bars are not intended to indicate properties which would be obtained from bars prepared from the castings which they represent, but to establish whether or not the metal from which they are cast is capable of giving the specified mechanical properties.<sup>83, 84</sup> In this respect they provide an expedient and economical means of checking the composition of the metal, which can be applied at greater frequency than chemical analysis. A caution worth giving is that work-hardening at the surface of a test-piece due to the use of blunt tools or to taking excessive cuts, can lead to considerably reduced test results.<sup>85</sup>

### 1. COPPER-TIN ALLOYS

The metallurgical examination of the copper-tin alloys for quality-control purposes presents considerable difficulties, particularly having regard to the influence of impurities. In Section V a description has been given of the way in which some of these affect the casting characteristics, while others, by their effect on the structure of the alloy, influence the strength. If adequate data were available about the effect of all these impurities, it might be possible to define limits for the amounts permissible, and to determine analytically the quantities present. Chemical analysis is, however, time-consuming and expensive, and although spectrographic techniques can be applied to most of the elements, facilities are not widely available, and methods are not always sufficiently accurate for the determination of the small quantities of some impurities considered to be harmful.

As regards the determination of mechanical properties, considerable difficulty is experienced in many foundries in casting from a single heat test-bars of uniform quality to give consistent results, and, in fact, results from a single set, often poured through a common runner, may be widely divergent. Because of this difficulty, specified minimum mechanical properties have been set at very low levels, with the consequence that metal of poor composition or high in impurity content can be passed on an apparently good test-bar result. It follows that specifications have amounted to little more than a statement of nominal composition, a situation which is not remedied, but is to some extent safeguarded against, by the fact that a considerable proportion of castings made are subjected to a pressure test or an operational test. Once techniques have been established by which consistent and representative results can be obtained, then realistic specification values can be set, and tests will indicate whether or not the metal is of satisfactory basic composition and is free from undesirable combinations of impurities.

Much work<sup>84, 86-88</sup> has been done in the past without the problem being solved, although in some foundries methods have been devised for improving consistency in results, and a study is being carried out at the present time by the B.N.F.M.R.A. The author has reported work in this field,<sup>85</sup> and has shown how greater consistency can be achieved, although not to the same degree

as that which can be obtained with high-tensile brass or aluminium bronze. This work, which was particularly related to leaded gun-metal test-bars, showed that the results obtained are directly related to the mode of solidification, and in particular to the formation of columnar grains in the test-section of the bar. A set of test results for LG 3 bars cast together as shown in Fig. 12 (Plate XLVIII) is given in Table VII, and the macro-

TABLE VII.—*Test-Bar Results \* on 86 : 7 : 5 : 2 Gun-Metal.*

	Tensile Strength, tons/in. <sup>2</sup>	Elongation, %
Upper . . . .	16.5	26 O.G.M.
Centre . . . .	15.9	25 O.G.M.
Lower . . . .	10.0	9

\* Triple bar (see Figs. 11 and 12, Plate XLVIII).

structures of the bars are illustrated in Fig. 11 (Plate XLVIII): the macrostructures of the centre and upper bars, which gave reasonable results, are columnar, while that of the lower bar, which gave a very poor result, is equiaxed. These results can be compared with those in Table VIII for bars cast in sets of three as individual bars

TABLE VIII.—*Test-Bar Results \* on 86 : 7 : 5 : 2 Gun-Metal.*

Casting Temp., °C.	Density, g./c.c.	Tensile Strength, tons/in. <sup>2</sup>	Elongation, %
1160	8.84	20.1	44
	8.85	19.9	40
	8.83	18.1	20
1120	8.77	17.3	23
	8.77	17.4	23
	8.79	17.4	24
1080	8.81	18.7	29
	8.80	17.2	21
	8.82	17.8	28

\* Single bars cast in groups of 3, (see Fig. 13, Plate XLVIII).

(Fig. 13, Plate XLVIII), showing that pouring temperature is not a very critical variable if a suitable design is used to promote the formation of columnar grains. With columnar structures the influence of gas in reasonable amounts is reduced and fairly consistent results have been obtained between three bars poured from the same heat with densities as low as 8.65 g./c.c., compared with a theoretical density of 8.91 g./c.c. The important factor is that the metal should enter the mould quietly, without turbulence, and with the minimum movement due to momentum after the metal is poured; if these conditions are not observed equiaxed grains are formed. In the author's view it is unreasonable to expect one test to divulge more than a limited amount of information, and the most that can be expected of the test-bar is to indicate in an economical and reasonably expeditious manner that basic composition is satisfactory and that the metal is reasonably free from undesirable impurities. Such a test would be acceptable to purchasers of both ingots and castings. Work on the correlation of structure and test-



bar properties of 85 : 5 : 5 : 5 alloy has been reported by Kura, Eastwood, and Doig.<sup>89</sup>

During recent years considerable discussion has taken place on "melt-quality tests", meaning tests of the metal before casting. The expression "melt quality" in this sense is extremely difficult to define, as instanced by the following definition by Baker, Upthegrove, and Rote:<sup>90</sup> "The term 'high melt quality' has come to mean melts which are so low in deleterious gas content and other impurities that the metal, as poured from the pot, is capable of producing superior castings, if the moulding sand and gating be correct. It is necessary, therefore, that a quality test be one which will evaluate the metal with respect to gas content." Although this definition mentions several important factors, the final emphasis is upon gas content. The American workers carried out a considerable amount of work to develop a fracture test,<sup>90-92</sup> discussed in a previous paper by the present author,<sup>85</sup> but the outcome was not successful. In this country, a Sub-Committee of the Institute of British Foundrymen has been working on melt-quality tests, and has been concerned mainly with tests which would disclose gas content. So far as is known, no satisfactory technique has yet been found. There is, however, a test devised by Ransley<sup>93</sup> in which a measured volume of an inert gas is circulated through the liquid metal from which dissolved hydrogen is picked up until constant conditions are attained, when the hydrogen content is measured by the change in electrical conductivity. This technique has been developed and satisfactorily used for light alloys, but it is probable that further developments will have to be introduced before the apparatus is suitable for use with copper alloys; in the author's view this is the most promising development so far recorded.

Various fluidity tests have been developed<sup>94, 95</sup> which might be suitable for the determination of the presence of those impurities which affect the casting characteristics of the metal. Kondic<sup>96</sup> has discussed this aspect of metal quality and has devised a "star" test which he claims is an improvement upon the well-known "spiral" test. The test depends upon the distance which the metal will flow from the centre radially along arms of different thicknesses. Clearly the mould has to be made with suitable precision, the CO<sub>2</sub> process being useful in this respect, and the pouring of the test-piece has to be under complete control. Unfortunately, the results of this test with copper-tin alloys appear to be influenced by variations in temperature within the degree of accuracy obtainable with temperature-measuring equipment normally used in the foundry, but with future developments in mind the "star" test should not be overlooked.

## 2. HIGH-TENSILE BRASS AND ALUMINIUM BRONZE

With the high-tensile brasses and aluminium bronzes there is less difficulty in setting a specification, since the influence of impurities is known and consistent test-bar results can be obtained. These results can expeditiously and economically indicate whether or not the basic composition is as desired, and reveal the presence of impurities.

The specifications included in B.S. 1400 for the high-tensile brasses admit considerable tolerances in chemical

composition, and it is by no means satisfactory in practice to allow the elements mentioned to be present in any combination within the permissible ranges. These specifications can be regarded only as indicating the levels of mechanical properties and the broad ranges of composition which embrace the various compositions used by specialist manufacturers.

For routine quality control in the foundry, two types of test have been described in detail by the author:<sup>85</sup>

### (i) *The Fracture-Bar Test*

In this test a sample is poured into a chill mould to produce a long test-piece, as shown in Fig. 14 (Plate XLIX). The metal is allowed to remain in the mould for 15 sec., when the bar is knocked out, picked up in tongs and held in the air for 45 sec., and then carefully quenched by dipping the ends into water alternately, and progressively more deeply, until the whole bar is immersed, so that the quenching process takes about 30-45 sec. The bar is then nicked across the centre with a cold chisel and broken and the fracture examined with a magnifying glass. It is important to control the times of the various operations, as any serious deviations can give misleading results. With the high-tensile brasses, the amount of zinc which it is necessary to add to produce the desired proportion of  $\alpha$  to  $\beta$  in the final slowly cooled alloy can be estimated from the colour and the number of the sparkling facets in the fracture. With the necessary experience, the alloy can be brought to within 5%  $\alpha$  (approximately  $\frac{1}{2}$ % zinc) of the required amount. The colour and degree of sparkle in the fracture is standard for an alloy of a given basic composition, but if this is materially altered, then the standard characteristics of the fracture correspondingly change. In the case of the aluminium bronzes differences in aluminium content of the order of  $\pm 0.5\%$  can be detected; while this is suitable for the purpose of a rough check, it is not sufficiently close for control purposes.

### (ii) *The Sand-Bar Test*

This test can be carried out before casting only in the case of melts in which the metal can be retained molten for about  $\frac{1}{2}$  hr. without risk of significant losses, particularly of zinc in high-tensile brasses. It is also useful as a test for checking metal after alloying or after casting in a way which is far more precise than the fracture-bar test, and can in fact yield more information than a tensile test. In this method, the metal is poured into a sand mould (normally made in core sand so that a stock of moulds can be maintained), with an open top, to provide a bar  $3 \times 1 \times 1$  in. The metal is allowed to stand in the mould for a specified time—this is 15 min. in the case of the high-tensile brasses but can be shorter for aluminium bronze; the bar is then knocked out and rapidly quenched and a microsection is prepared. The proportions of phases such as  $\alpha$  to  $\beta$  in high-tensile brasses can be measured using a suitable attachment to the microscope stage.<sup>97, 98</sup>

This test discloses not only the basic structure but the amount and distribution of the iron-rich and other phases normally found, and the presence of impurities, such as lead, which can be seen under the microscope. In the case of high-tensile brass the proportion of  $\alpha$  to  $\beta$  in the microstructure of the sand bar is related to the propor-

tion of  $\alpha$  to  $\beta$  in the casting: this relationship can be accepted as varying from approximate equivalence for light castings to a maximum of 10% more  $\alpha$  in heavy castings than in the bar. On this basis the quality of the metal already cast can be assessed or additions can be made to metal that is being held molten. As a close approximation—the exact equivalence depends upon the composition—it can be taken that an addition of 1% zinc (1% of the charge weight) decreases the proportion of  $\alpha$  by 7%.

The methods described, when used for the correction of composition of high-tensile brass before casting, take into account variations in all those elements which influence the final proportion of  $\alpha$  to  $\beta$  in the microstructure, and variations from the nominal aluminium and tin contents are accordingly compensated for by additions of zinc, a correction which is permissible within certain limits. If, of course, either of these elements deviates significantly from the required composition, the properties of the alloy are affected, but this can be disclosed only by chemical analysis. A copper determination, which is sometimes used as a check before casting, is unreliable in that it is assumed in using it that the basic composition apart from the zinc is correct, and that the total deviation in copper content is due to zinc loss during melting: in view of the high zinc equivalent of aluminium, a small divergence of aluminium content from the nominal value could lead to a result significantly in error.

As far as the aluminium bronzes are concerned, a fairly close assessment of aluminium content can be made from the microstructure of the sand bar (to within  $\pm 0.25\%$ ), the difference between the microstructure of the sand bar and that of the casting being related to the time for which the bar is allowed to remain in the mould before quenching.

For the determination of gas content, the equipment developed by the B.N.F.M.R.A.,<sup>99</sup> based on the Straube-Pfeiffer test, and now marketed commercially, is normally used for aluminium bronze, but is not suitable for high-tensile brass. The sample is allowed to solidify under reduced pressure; any gas present comes out of solution and causes the skin formed over the surface of the sample to rise. Standard conditions are established to indicate when the gas content exceeds the critical level. A simplified version of the vacuum-extraction equipment, described by Eborall and Ransley<sup>100</sup> and by Ransley and Talbot<sup>101</sup> as adequate for normal purposes associated with production, can be set up for absolute measurements; there is, of course, the limitation that results could not normally be made available before casting the metal, but the equipment can be used for all copper-base alloys.

## IX.—MODE OF SOLIDIFICATION

The cast copper alloys with which this paper is concerned can be divided into two groups, alloys such as the high-tensile bronzes and aluminium bronzes which solidify over a short temperature interval, and alloys based on copper-tin which solidify over a long temperature interval. This difference in characteristic has a

marked effect on the mode of solidification of the two groups of alloys, in the absence of certain special circumstances referred to later.

In the case of the high-tensile bronzes and aluminium bronzes solidification begins with the nucleation of crystals at the mould surface, and is followed by progressive skin formation; in most castings, apart from those with very heavy sections, solidification proceeds with only a small distance between the isothermals, corresponding to the boundaries of totally solid and totally liquid metal. The final metal to solidify, therefore, is normally situated in the centres of sections, so that, by the judicious use of feeders and chills to promote directional solidification, castings can be produced sound and free from shrinkage cavities.

In the copper-tin alloys, dendrites begin to grow from the mould surfaces and, if the temperature gradients are sufficiently marked—as they are near the mould surfaces in most castings—columnar grains develop. The extent to which these grow is dependent upon the temperature gradients and the metal temperature, for as grains are nucleated in the inner mass of the liquid further growth of the columnar grains is inhibited. As dendrites are formed in the mass of the liquid they are able to move with the liquid during that stage known as “mass-feeding”, which can continue until the dendrites have become large and solidly packed, when further feeding can take place only by a movement of the liquid metal between the dendrites. As the interstices become narrower bridging occurs, and isolated layers of metal solidify without feeding, to leave small shrinkage cavities. The degree of unsoundness, which is unavoidable with this type of solidification, depends upon the availability of liquid metal from adjacent zones of the casting and the extent to which further movement is prevented by the presence of oxide films or by the evolution of gas during solidification. If excessive gas is present, the metal remaining liquid may be exuded as an inverse segregate,<sup>102</sup> or “tin sweat”, an effect to which alloys of higher lead content are particularly susceptible. According to the mode of solidification envisaged, the outer skin of the casting consists of columnar grains and the core of equiaxed grains. By virtue of the conditions under which the columnar grains are formed, the metal in the zones in which they develop is relatively sound and pressure-tight and of high strength. The desirability of promoting the formation as far as possible of columnar structures is clear, whether pressure-tightness<sup>103, 104</sup> or strength alone is required.

In the hope of facilitating the production of pressure-tight castings in these alloys, the B.N.F.M.R.A. has carried out a research on grain refinement.<sup>103</sup> With those light alloys having long solidification ranges grain refinement had been shown to have a beneficial effect on mass-feeding, to reduce the tendency to hot shortness and improve the strength by producing a more finely distributed porosity. The work was successful in as much as methods were found of producing grain refinement and of reducing the overall level of porosity, but the castings were less pressure-tight. Porosity was distributed throughout the cross-section of the poorly fed regions, voids were mostly intergranular, many of them forming in layers perpendicular to the direction of feeding, and the metal near the surfaces of the casting was generally unsound, in contrast to what is normally found in coarse-



grained material. The Association has further work in hand to study the casting characteristics of these alloys with particular reference to the factors affecting the incidence of harmful forms of porosity, and with a view to selecting alloy compositions which with economic foundry techniques will give high-quality castings.

The growth of columnar grains in the copper-tin alloys depends largely on increasing the rate of cooling, or the steepness of the temperature gradients, so as to reduce the influence of the wide temperature interval through which the alloy solidifies, and to close the gap between the isothermals bounding totally solid and totally liquid metal. Under these conditions, the mode of solidification begins to resemble that of the aluminium bronzes and high-tensile brasses. Conversely, in the aluminium bronzes and high-tensile brasses under conditions of very slow cooling, such as occur in very heavy sections, the normal influence of the narrow temperature interval during which solidification occurs is lost and the gap between the isothermals bounding totally solid and totally liquid metal very considerably widens, with the result that features normally associated with the copper-tin alloys may be found. For example, normal segregation is common in high-tensile brasses under these conditions and may become marked, and in the presence of excessive amounts of dissolved gas inverse segregation can occur. The alloys high in tin content, of the order of 1%, are, for reasons described in Section II, particularly susceptible to these effects, with the possible incidence of an inverse segregate of  $\beta/\gamma$  structure arising from an alloy solidifying in the casting as  $\alpha/\beta$ . Another feature common to these alloys as they solidify in heavy sections, which is revealed more markedly by the high-tensile brasses than by the aluminium bronzes, is the segregation under the influence of gravity of the first crystals formed, carrying with them the iron-rich grain-refining nuclei about which they form. Consequently, the last liquid to solidify is relatively close to the upper surface of the mould and is deficient in these nuclei, and coarse grains therefore develop.

Both the special features just described are illustrated in Fig. 15 (Plate XLIX); the normal coarse-grained zone and the abnormal inverse segregate can be seen, (a) showing a complete section, while (b) shows the upper part and top surface of the section, both being the way

the casting is  $\alpha/\beta$ , the structure of the inverse segregate is  $\beta$  and  $\beta/\gamma$ .

#### X.—THE CONTROL OF CASTING QUALITY: FACTORS OTHER THAN METAL QUALITY

The founding of the copper-tin alloys is a craft practised for thousands of years, and only recently has the technologist probed its secrets. The high-tensile brasses and aluminium bronzes have been developed in comparatively recent years, and the establishment of foundry techniques for them responds to a logical approach. The factors influencing the satisfactory casting of the copper-tin alloys, however, are relatively so complex, owing to the long solidification range and the influence of gases, that even now much remains to be learned. Consultation between the designer and the foundryman, as is the case in the aircraft industry, is most desirable; many of the difficulties which have to be overcome in the foundry could be obviated at the design stage.<sup>105</sup> It is also necessary to emphasize that mechanical properties laid down for specification purposes will not necessarily be realized in all parts of the casting.<sup>106, 107</sup>

The measurement of temperatures presents a problem in the foundry working with copper-base alloys. Temperature control is an essential in the control of quality, but completely reliable and serviceable equipment is not yet available. The now commonly used Chromel/Alumel thermocouples, swaged into heat-resisting steel tips, have to be rechecked frequently and give a variable life before failure, which does not depend only upon the temperatures at which they are used. They are expensive, and deliveries, which are dependent on supplies of steel, cannot always be relied upon. An alternative is to use a platinum/platinum-rhodium couple, protected by a short graphite sheath attached to a steel tube. By the use of a device for coiling surplus wire in the head of the instrument, only a short portion has to be discarded when failure occurs, and it is not necessary to replace the entire length of the couple. The graphite sheaths are fragile and burn through in air fairly quickly, so that even though it is possible to economize in wire, the method is expensive and by no means trouble-free. Techniques are being currently considered which eliminate the immersion of protected thermocouples in the metal and depend instead upon the measurement of radiation from the bottom of a closed tube; in one case the heat is focused on to fine thermocouples in a rather delicate lightweight head connected to a scale through suitable amplifying equipment, while in the other case the infra-red radiation falls on a photoelectric cell connected to a scale through an amplifier.

Mention should be made of the monograph by Ruddle<sup>108</sup> on "The Solidification of Castings", in which the subject is considered both empirically and fundamentally, and to a paper by the same author on "The Running and Feeding of Castings".<sup>109</sup> Other references are given in the Introduction. A relatively recent development, important in the economic production of castings in all the copper-base alloys, has been the introduction of exothermic and porous plaster sleeves for feeders, about which a number of papers have been written.<sup>110-112</sup> A report by I.B.F. Sub-Committee T.S. 35<sup>113</sup> on "Flow of Metal", including an excellent

TABLE IX.—Analyses Taken at Various Positions Across a Heavy Section of a High-Tensile Brass Casting.\*

	A	B	C	D	E
Copper, % . . .	54.78	55.37	54.99	55.75	55.69
Zinc, % . . .	42.70	42.33	42.64	41.83	41.88
Aluminium, % . .	0.13	0.18	0.16	0.18	0.19
Manganese, % . .	0.24	0.20	0.24	0.22	0.22
Tin, % . . .	1.39	0.98	1.10	1.02	1.04
Iron, % . . .	0.60	0.85	0.74	0.94	0.87
Lead, % . . .	0.03	0.01	0.01	0.01	0.01

\* See Fig. 15 (Plate XLIX).

up as cast. The results of chemical analyses of specimens taken at the points indicated in the illustration are given in Table IX. The photomicrograph (Fig. 16, Plate L) shows that although the general structure of

film, is a valuable contribution; similar work in America, using water and Wood's metal, has also been filmed and reported.<sup>114</sup> The B.N.F.M.R.A. have in hand a research into running and gating methods, and Ruddle has published a review of the literature.<sup>115</sup>

It is clearly advantageous to have a "Methods Foundry" in which techniques can be developed and set before work is put into production on the shop floor.

## 1. COPPER-TIN ALLOYS

### (a) Sand Casting

The significance of mode of solidification has been discussed, and so has the question of whether castings are required to have maximum strength or to be pressure-tight, and the desirability of inducing as far as possible the formation of columnar structures has been indicated. The characteristics of the constitution of the alloys which govern the mode of solidification also affect the coarseness and distribution of the ( $\alpha + \delta$ ) eutectoid in the microstructure, and foundry techniques which favourably influence the one similarly affect the other. It has also been shown in the work reported on test-bars that columnar structures are less sensitive to gas content than those which are equiaxed, which is consistent with the way in which they develop.

The formation of the desirable columnar structure is favoured by the avoidance of turbulence during casting, and by pouring at such a temperature that the metal as far as possible comes to rest in each part of the mould before its temperature has dropped sufficiently for nuclei to separate in the mass of the metal; also, the higher the casting temperature, the more favourable are the temperature gradients set up. Local overheating in the

that much success has been due to the skill of the operatives who pour castings. In these days of diminishing numbers of skilled men it is necessary to devise running systems which remove the need for the skill; the B.N.F.M.R.A. is carrying out research into gating systems, while a paper has been published by Kura and Eastwood on the "Effects of Gating Practice on Leak Tightness of Gun-metals".<sup>116</sup> A final point to be made concerning columnar structures is that injudicious machining allowances can lead to their removal, and if the castings have a core of equiaxed structure, strength can be impaired and pressure-tightness reduced to the extent that castings otherwise pressure-tight may leak.

The principles generally adopted with copper-tin alloy sand castings are to use feeding ingates at suitable heavy sections, which assist in promoting directional solidification, and to employ feeders or chills<sup>77, 117</sup> on other heavy sections. Because of the manner in which these alloys normally solidify, the apparent shrinkage is not as high as with the high-tensile brasses and aluminium bronzes (in fact, the actual freezing shrinkages are of the same order, see Table X), and the use of heavy feeders and the free use of chills on heavy sections is not necessary with the copper-tin alloys; in fact, excessively large feeders can lead to castings being more, instead of less, porous. It is inadvisable to employ exothermic feeding sleeves, as, owing to the ready solubility of gas in the metal and the long solidification range, these are likely to promote gas unsoundness, but plaster insulating sleeves are very effective. It was common practice in many foundries years ago to pour copper-tin alloys using high metallostatic pressure, and current knowledge explains how this assists mass-feeding and interdendritic feeding, thereby promoting higher density. In many foundries this practice is falling a victim to economic factors, and foundrymen would be wise to recall the technique, particularly for intricate or pressure-tight castings.

The desirability of promoting columnar structures has been pointed out, but in a large proportion of industrial castings at least the core structures are inevitably equiaxed. So that these structures should be as strong and as pressure-tight as possible, it is necessary to avoid local concentrations of porosity and to ensure that the general level is low. The principles adopted for feeding have been indicated, and in earlier sections techniques have been described for reducing the gas content of the metal to a minimum, although it has also been pointed out that under certain conditions a small gas content, introduced during melting or by metal/mould reaction, is desirable.

### (b) Chill Casting

The techniques recommended for the manufacture of chill-cast solid and cored stick have been clearly and concisely set out in a booklet by the Tin Research Institute,<sup>39</sup> and very fully described by Hanson and Pell-Walpole.<sup>6</sup> Cast-iron moulds are normally used, although copper moulds are recommended, and these are usually split so that they can be cleaned and dressed. For dressing, aluminium powder suspended in a resinous carrier has been suggested, although various oil-, water-, or spirit-base dressings are frequently used. Wrong choice of, or lack of care in the application of, dressings can lead to blowing from the mould surface to form large gas holes,

TABLE X.—Shrinkage Characteristics of Copper-Base Casting Alloys. (Baker.<sup>118</sup>)

Alloy	Freezing Shrinkage Volume Change, Liquid to Solid, Expressed as a Percentage of Volume at Room Temperature	Freezing Range, °C.	Ref.
Aluminium bronze (90 : 10)	4.6	10	122
Manganese bronze (high-tensile brass)	5.2	30	122
92 : 8 Tin bronze	5.8	200 approx.	123
85 : 5 : 5 : 5 Leaded gun-metal	5.6 7.0	675 approx.*	124 122

\* Most of the metal freezes over a range of the order of 200°–250° C., the very extended range quoted being due to the residual lead, which freezes at 327° C.

mould should be avoided as far as possible. It has not been common practice with these alloys to endeavour by design of running and gating systems to achieve quiet entry of the metal into the mould, and there is no doubt



subcutaneous gas porosity in the form of small holes, surface inclusions, and "tin sweat".

The moulds are poured vertically, usually through a carefully prepared tundish with one or more (in the case of cored sticks) holes to control the rate of flow of the metal, which should be poured hot at the minimum rate that will enable the mould to be filled without cold shuts. Hanson and Pell-Walpole<sup>6</sup> quote a formula for the calculation of pouring rate and recommended temperatures for various alloys. The phosphor bronzes lend themselves readily to this method of casting, but more difficulty is experienced with the gun-metals, in particular with the lead-free gun-metals, where an increased pouring rate is necessary;<sup>31</sup> this is associated with the effects of zinc in these alloys already described.

In recent years a technique for the semi-continuous casting of chill-cast solid and cored stick has been worked out by the Tin Research Institute, and further developed to a production scale by a number of companies. Like the patented Asarco process<sup>40, 41</sup> for continuous casting, this depends upon feeding molten metal through a specially designed die in a carefully selected grade of graphite, and quenching the stick by jets of water. Apart from points of detail, the important difference is that in the Tin Research Institute method limited quantities of metal are poured at a time, while in the Asarco process the metal can be continuously poured in an inert atmosphere from a large holding and pouring vessel fed from a separate furnace. An Asarco plant is now operating in this country. Solid or cored sticks prepared by these methods exhibit markedly better properties than are normally found in sticks chill-cast by earlier methods.

The copper-tin alloys are not die-cast in the normal sense because of their hot shortness, although simple forms are sometimes cast in metal moulds. A process known as "form-casting" was patented<sup>119</sup> in 1947, by which a cast die is prepared, normally in aluminium bronze, so that simple castings of good surface finish and reasonable dimensional accuracy can be obtained economically when the numbers required would not justify the cost of sinking a die.

## 2. HIGH-TENSILE BRASSES AND ALUMINIUM BRONZES

### (a) Sand Casting

Foundry techniques for these alloys have to be directed towards avoidance of the entrapment of oxide films, which are readily formed, and towards ensuring directional solidification so that adequate feeding takes place to offset the high shrinkage that occurs during solidification. While the high-tensile brasses are less troublesome than the aluminium bronzes, the principles are the same for both groups, and it is therefore convenient to consider them together.

To avoid oxide inclusions it is necessary to avoid turbulence, and for this reason bottom pouring is adopted. Precautions have to be taken to keep the downstick full, and although a tapered variety is preferable to ensure a full downstick and a clean flow, parallel downsticks with chokes are frequently employed. The disadvantage, however, arises with the parallel downsticks that air can be induced into the metal stream to form oxides. A sump under the downstick is valuable

in steadying the metal, and usually between the downstick and the gate to the casting a suitable dirt trap is incorporated. Entry to the mould through a small gate, with the metallostatic pressure producing jets or fountains of metal, is clearly undesirable. There is every advantage in casting the metal as quickly as possible, compatible with the avoidance of turbulence. It is important to avoid as far as possible streams of metal meeting, as this frequently results in the entrapment of oxide films. Success, therefore, lies in devising suitable running and gating systems.

Directional solidification is achieved by the use of adequate feeders on heavy sections and by the free use of chills. A difficulty arising from the use of bottom pouring is that the metal reaching the feeders is cold. The risks involved in topping up feeders with hot metal cannot be over-emphasized; unless proper precautions are taken the metal poured into them does not stay there but penetrates deeply into the mould. In order to maintain feeders open sufficiently long to feed the casting adequately, it has been necessary in the past to make them very large; their total weight might be of the same order as the weight of the casting, or even higher. The size can be very considerably reduced by making use of porous-plaster insulating sleeves, which retain the heat and reduce the necessity for large size. A disadvantage is that with aluminium bronze such as AB 2, cast at high temperatures, the temperature of the metal entering the sleeve tends to exceed 1160° C., above which an energetic exothermic reaction is likely to take place between the metal and the plaster, causing the latter to disintegrate and to become ineffective as an insulator. A better alternative is the use of exothermic sleeves, so that the temperature of the cold metal reaching the feeders is considerably raised. One important precaution has to be taken in using exothermic sleeves, because the exothermic reaction can lead to gas pick-up in the feeder. This can result, in the case of the aluminium bronzes, in gas porosity in the casting under the feeder unless a suitable distance is allowed between the sleeve and the surface of the casting.

### (b) Chill Casting

These alloys, as well as straight brasses, are all suitable for die-casting, although, because of the high casting temperatures involved, the wear on the iron or heat-resisting steel moulds is considerable, particularly in the case of the complex aluminium bronze AB 2. The high-tensile brass normally die-cast is HTB 1. As in the case of sand casting, the techniques used are directed towards achieving directional solidification and the avoidance of the entrapment of oxide films. Bottom pouring and choked runners are normal, and adequate feeders have to be provided: refractory sleeves are sometimes used to delay solidification.

In the case of the brasses, a build-up of a drossy mixture of zinc and zinc oxide occurs on the walls of the die, which has to be frequently removed. Whereas dies are normally dipped in a suspension of graphite in water, both to cool them and to provide a suitable dressing, special dressings have been developed to prevent this build-up.<sup>120</sup>

A booklet of general interest on die-casting has been published by Penny.<sup>121</sup>

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# CONTROL OF QUALITY IN THE PRODUCTION OF NICKEL ALLOY SAND CASTINGS\*

1751

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## SYNOPSIS

An account is given of the effects of small variations in composition on the mechanical properties of alloys of nickel with carbon, silicon, copper, chromium, molybdenum, tungsten, and tin, and containing also iron and manganese. Small contents of sulphur and lead are shown to be deleterious. Their effects are less pronounced in nickel-chromium than in nickel-copper alloys. Some data are given on the factors affecting welding properties and castability.

The choice of melting furnaces, refractory linings, and raw materials is discussed. Descriptions are given of melting procedures for electric-induction and arc furnaces, including the use of "boiling" and oxygen lancing for degassing and refining, and reference is made to melting in other types of furnace. It is shown that, by oxygen lancing nickel-copper and nickel-chromium-iron alloys, a high level of mechanical properties is obtained from scrap-metal charges, and that the weldability of the nickel-copper alloys is also improved. Techniques of alloying, deoxidation, and sulphur control are described.

The high melting point and the high liquid and solid contraction of nickel-base alloys, combined with their relatively low strength at temperatures immediately below the solidus, are shown to call for the use of highly refractory moulding sands, substantial feeder systems, and mould designs permitting unhindered contraction of the metal, in both the liquid and the solid state.

## I.—INTRODUCTION

NICKEL alloy sand castings are frequently used under corrosive conditions and are often required to be pressure-tight to corrosive fluids. In addition, they are often exposed to high temperatures and should be amenable to welding. In many applications, reliance is placed also on their stress-carrying capacity.

To meet these exacting requirements, the castings must be of good quality, and not only be free from normal casting defects, viz. cracks, porosity, surface laps, &c., but have a homogeneous structure and contain no undesirable constituents which could impair their corrosion-resistance, mechanical properties, or weldability.

In the discussion of control of quality which follows, emphasis is placed on those factors which are specially important in the production of nickel alloys; relatively little attention is given to the general principles of good founding that are applicable also to other alloys.

The paper begins with an account of the compositional factors affecting the properties of sand-cast nickel alloys. Subsequently, a description is given of methods of achieving the desired control, particular attention being devoted to melting procedures.

Table I gives the nominal compositions of the principal nickel-base alloys manufactured as sand castings, together with their approximate freezing ranges and pouring temperatures.

## II.—MECHANICAL PROPERTIES

Typical mechanical properties, at room temperature, of the sand cast-nickel alloys are given in Table II, and

the effects on mechanical properties, at normal and at elevated temperatures, of certain variations in composition are described below.

### 1. VARIATIONS IN CARBON CONTENT

Relatively small variations in carbon content have marked effects on the structure and properties of nickel alloys.

The solubility of carbon in pure, liquid nickel is 2.2% at the eutectic temperature of 1315°C.<sup>1</sup> and the solid solubility decreases from about 0.5% at that temperature to about 0.2% at room temperature. In cast Nickel, ‡ carbon in excess of about 0.3% occurs in flake form, and for ordinary purposes the aim is to secure a carbon content of 0.20%.

In general, carbon is less soluble in nickel alloys than in nickel, e.g. in Monel free graphite is present at carbon contents higher than approximately 0.15%, while in "S" Monel, containing 30% copper and 4% silicon, free graphite appears in the microstructure at carbon contents of the order of 0.1%.

The effects of variations in carbon content on the room-temperature mechanical properties of Monel are shown in Fig. 1. From these data it is clear that the optimum carbon content with respect to strength and ductility is about 0.2%, but the steep fall in impact strength with increasing amounts of carbon requires that a somewhat lower maximum be specified. A nominal carbon content of 0.15% is usually desirable.

The nominal carbon contents given for the other alloys in Table I are derived from similar considerations, and in all cases they represent a practical compromise among

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† The Mond Nickel Co., Ltd., Birmingham.

‡ In this paper, nickel denotes the pure element and Nickel the first material in Table I, containing significant amounts of alloying elements.

TABLE I.—Chemical Compositions of Sand-Cast, Nickel-Base Alloys.

Alloy	C, %		Si, %		Mn, %		Cu, %		Fe, %		Mo, %		Others, %		Mg, %		S, %	Pb, %	Freezing Range, °C.	Pouring Temperature, °C.	
	Nominal	Range	Nominal	Range	Nominal	Range	Nominal	Range	Nominal	Range	Nominal	Range	Nominal	Range	Nominal	Range	max.	max.	°C.	Heavy Section	Light Section
Nickel	0.20	0.10-0.30	1.5	1.0-2.0	1.25	1.0-1.5	...	0.3 max.	...	1.0 max.	...	...	...	...	0.10	0.08-0.12	0.05 max.	0.005 max.	1430-1350	1510	1590
Graphitic Nickel	1.2 2.0 †	1.0-2.5 2.0-2.5	2.0	1.8-2.2	1.5	1.3-1.7	...	0.3 max.	...	1.0 max.	...	...	Sn 2.5-4.0 (nominal 3.0)	...	0.15	0.10-0.20	0.05 max.	0.005 max. ‡	1430-1340	1430	1530
Nickel-Copper-(1.0% Silicon) (Ordinary Monel §)	0.15	0.10-0.25	1.0 †	0.5-1.5	1.0	0.5-1.5	30	28-32	...	3.0 max.	...	...	...	...	0.10	0.08-0.12	0.05 max.	0.005 max.	1350-1315	1500	1560
Nickel-Copper-(2.75% Silicon) ("H" Monel)	0.10	0.15 max.	2.75	2.5-3.0	1.0	0.5-1.5	30	28-32	...	3.0 max.	...	...	...	...	0.10	0.08-0.12	0.05 max.	0.005 max.	1320-1290	1470	1530
Nickel-Copper-(4.0% Silicon) ("S" Monel)	0.05	0.10 max.	4.0	3.5-4.5	1.0	0.5-1.5	30	28-32	...	3.5 § max.	...	...	...	...	0.10	0.08-0.12	0.05 max.	0.005 max.	1290-1260	1420	1500
Nickel-Molybdenum-Iron (Hastelloy "B" **)	0.05	0.12 max.	0.5	1.0 max.	0.5	1.0 max.	...	...	6	4-7	28	26-30	W 4.75-5.25 (nominal 5.0)	Cr 15.0-17.0 (nominal 16.0)		...	0.05 max.	0.005 max.	1350-1320	1500	1560
Nickel-Molybdenum-Chromium-Tungsten (Hastelloy "C" *)	0.05	0.12 max.	0.5	1.0 max.	0.5	1.0 max.	...	...	5	4-6	17	16-18	...	...		...	0.05 max.	0.005 max.	1305-1270	1490	1550
Nickel-Chromium-Iron (Inconel †)	0.10	0.3 max.	1.0	0.5-2.0	0.7	0.5-1.0	...	0.25 max.	7	5-10	...	...	...	Cr 12-15 (nominal 14.0)		...	0.05 max.	0.005 max.	1400-1375	1530	1600

\* Monel, Inconel, and Hastelloy are registered trade marks.

† In the absence of tin, the alloy should contain &lt;2.0% carbon, if the best anti-galling properties are required.

‡ For optimum weldability, the silicon content should not exceed 1%.

§ 2.5-3.5% iron for maximum hardness.

|| Treated with calcium. Normal addition = 0.05-0.10% calcium.

¶ For graphite in spheroidal form.



the relevant factors—castability, mechanical properties, &c.

As stated above, carbon in excess of the solubility limit is precipitated in flake form, but the presence of such elements as magnesium tends to transform the excess carbon into a nodular or spheroidal form. In Graphitic

TABLE II.—Typical Room-Temperature Mechanical Properties of Sand-Cast, Nickel-Base Alloys.

Alloy	0.1% Proof Stress, tons/in. <sup>2</sup>	Yield Point, tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	Elongation, % on 2-in. Gauge Length	Brinell Hardness No.
Nickel	7.5	9–13	20–27	10–30	80–120
Graphitic Nickel	Tin-free	...	9	27	25
	3% tin	...	18	31	15
Monel	10	11–15	28–33	25–40	100–150
“H” Monel	15	18–23	33–40	8–15	230–280
“S” Monel	...	40–45	40–45	1–4	275–350
Hastelloy “B”	...	24–26	34–36	6–10	180–230
Hastelloy “C”	...	24–26	32–36	5–10	180–230
Inconel	...	15–20	32–35	10–20	160–200

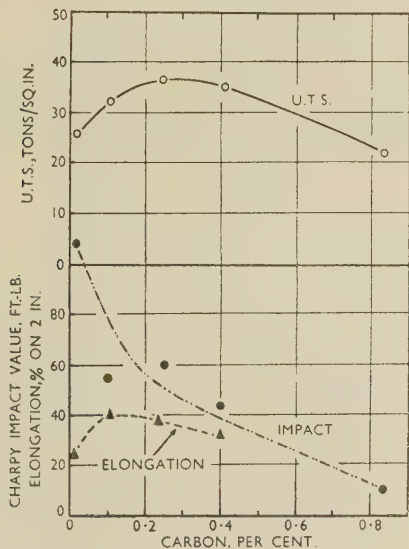


FIG. 1.—The Effects of Carbon Content on the Mechanical Properties (at Room Temperature) of Cast Monel. (After Eash and Kihlgren.<sup>4</sup>)

Nickel, for example, a suitable excess of magnesium over sulphur produces a structure in which all the free graphite is in the spheroidal form (Fig. 12, Plate LI).

2. VARIATIONS IN SILICON CONTENT

Additions of silicon to nickel-base alloys are useful for deoxidation and for promoting good castability, but they also have important effects on mechanical properties. The data in Fig. 2 illustrate the need for restraint in adding silicon to Monel, in view of the sharp fall in ductility at silicon contents higher than approximately 2%.

The effects of silicon in Monel are enhanced by a high copper content. Heats having copper contents at the upper limit of the recommended range, 28–32%, possess

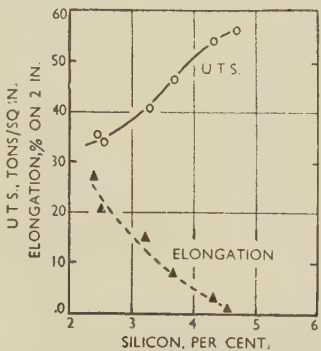


FIG. 2.—The Effects of Silicon Content on the Mechanical Properties of Cast Monel. (After Eash and Kihlgren.<sup>4</sup>)

somewhat greater hardness and yield and ultimate tensile strengths and, usually, lower ductility, than heats containing approximately 28% copper. These effects,

TABLE III.—The Effects of Varying Copper Content on the Tensile Properties of Cast Monel. (Eash and Kihlgren.<sup>4</sup>)

Heat No.	Composition, %					Yield Strength, tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	Elongation, % on 2 in.	Brinell Hardness No.
	C *	Si	Fe *	Cu *	Ni				
3	(0.05)	2.46	2.15	(28.5)	Bal.	17.7	35.6	26.5	157
12	(0.05)	2.41	(1.25)	(32.5)	Bal.	21.7	41.7	28.5	170
6	(0.05)	3.22	(1.25)	(28.5)	Bal.	26.6	41.2	13	195
13	(0.05)	3.20	(1.25)	32.3	Bal.	33.6	41.7	5	229

\* Figures in parentheses are nominal values.

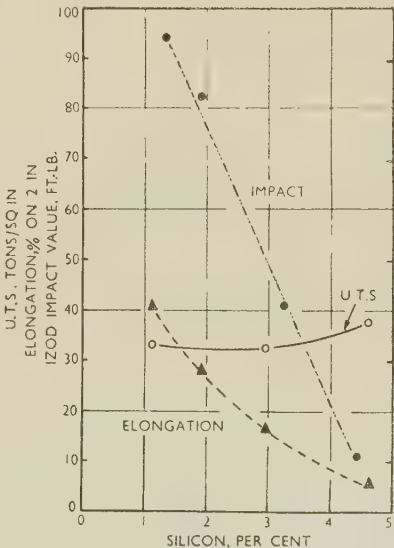


FIG. 3.—The Effects of Silicon Content on the Mechanical Properties of Cast Inconel.

which are due to decreased solubility of silicon and the resulting precipitation of a hardening phase at higher copper contents, are illustrated in Table III.<sup>4</sup>

Typical data for sand-cast Inconel made by remelting wrought Inconel bar are presented in Fig. 3. Increased silicon contents may be used in Inconel, to promote improved casting properties, but account must be taken of the concomitant reduction in ductility and impact strength.

### 3. EFFECTS OF SULPHUR

Sulphur is readily absorbed by nickel, and forms with nickel a eutectic containing 21.5% sulphur, which melts at 645° C. In castings, the eutectic occurs in the grain boundaries, and results in reduced tensile properties, particularly at high temperatures. Similar impairment of properties is produced by sulphur in the nickel-copper alloys.

The practical effects of sulphur contamination are not only to cause reduced mechanical properties in the finished castings, but also to promote hot tearing and poor weldability. It is customary to restrict the sulphur content of nickel alloy castings to a maximum of 0.05%, as stated in Table I, but the presence of even lower percentages of sulphur (e.g. 0.01–0.05%) in nickel or Monel is sufficiently damaging to necessitate corrective treatment with manganese and magnesium.

While additions of manganese are beneficial, as the result of the formation of manganese sulphide inclusions in place of grain-boundary films, magnesium has a still stronger affinity for sulphur and produces a sulphide of an innocuous type. The effects, on room-temperature

TABLE IV.—*The Effects of Magnesium on the Mechanical Properties of Monel Containing 0.05% Sulphur. (Based on Eash and Kihlgren.<sup>4</sup>)*

Mechanical Properties at Room Temperature	No Magnesium	0.1% Magnesium
Yield point, tons/in. <sup>2</sup> . . . . .	13.4	14.1
U.T.S., tons/in. <sup>2</sup> . . . . .	14.1	32.9
Elongation, % . . . . .	4.0	35.0
Charpy Impact Value, ft.-lb. . . . .	16.0	49.0
Brinell Hardness No. (1000-kg. load)	108	135

mechanical properties, of magnesium additions to sulphur-containing Monel are given in Table IV. Typical microstructures are illustrated in Figs. 13 and 14 (Plate LI). In nickel-chromium alloys, the effect of sulphur is relatively smaller, owing to the formation of less harmfully distributed chromium sulphide. The metallographic features of the phenomena associated with sulphur in nickel alloys have been described in detail in the literature.<sup>3</sup>

### 4. EFFECTS OF LEAD

Contamination of nickel alloys with lead up to about 0.1% has relatively small effects on the room-temperature tensile properties, but it exerts a strongly deleterious effect on properties at higher temperatures. Lead contamination engenders hot shortness, and the presence of lead often accentuates the effects of unsatisfactory mould design, by producing hot tears. As with sulphur contamination, the effects of lead are more striking in nickel-copper alloys than in nickel-chromium alloys. Tensile test data for lead-contaminated Monel and Inconel, at room temperature and at 425° C., are given in Figs. 4–7.

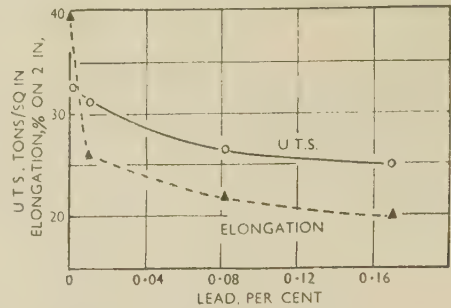


FIG. 4.—The Effects of Lead Content on the Tensile Properties of Cast Monel at Room Temperature. (After Eash and Kihlgren.<sup>4</sup>)

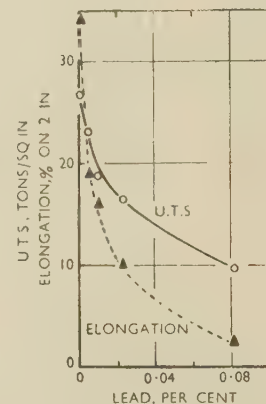


FIG. 5.—The Effects of Lead Content on the Tensile Properties of Cast Monel at 425° C. (After Eash and Kihlgren.<sup>4</sup>)

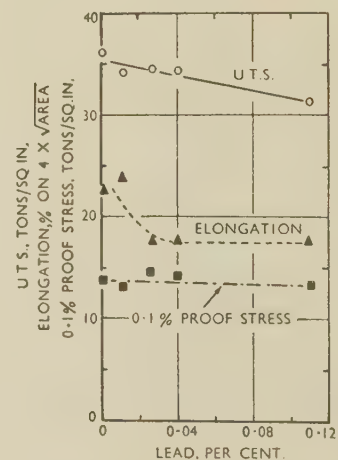


FIG. 6.—The Effects of Lead Content on the Tensile Properties of Cast Inconel at Room Temperature.

The upper limit of lead content in cast nickel alloys is generally specified as 0.005% (Table I).

The harmful effects of lead at elevated temperatures can be offset by additions of zirconium<sup>5</sup> as shown in Fig. 8. It has been demonstrated,<sup>4</sup> however, that additions of zirconium impair the room-temperature tensile strength and ductility, as well as adversely affecting



machinability and welding properties. It is desirable, therefore, to avoid lead contamination rather than to use zirconium as a palliative after contamination has occurred.

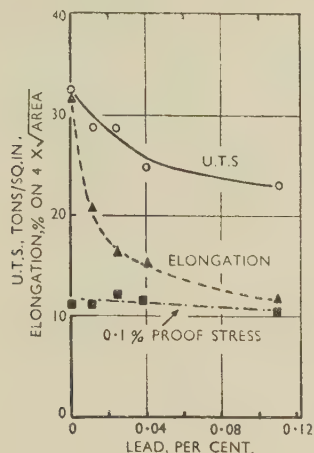


Fig. 7.—The Effects of Lead Content on the Tensile Properties of Cast Inconel at 425° C.

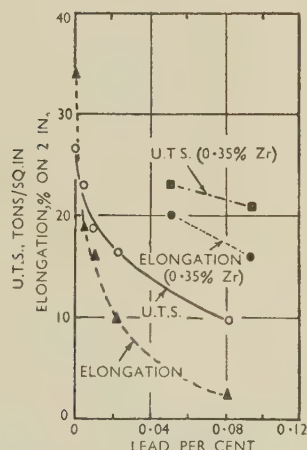


Fig. 8.—The Effects of Zirconium Additions on the Mechanical Properties of Lead-Contaminated Cast Monel at 425° C. (After Eash and Kihlgren.<sup>4</sup>)

### III.—WELDING PROPERTIES

Satisfactory welding properties are required in nickel alloy castings for two purposes: (a) repair of minor damage or correction of defects, and (b) fabrication for service.

Only limited data on the weldability of nickel-base castings are available in the literature. Tests on cast Monel, welded by the metallic-arc process, have, however, shown that cracks frequently occur on the surface and also in the body of the casting adjacent to the weld metal (Fig. 15 (a), Plate LI). Normal variations in composition, within the ranges given in Table I, have no appreciable influence on welding properties, but high silicon contents, e.g. 2.5% and above, or phosphorus and lead contents exceeding approximately 0.05 and 0.005%, respectively, impair weldability. Small amounts of boron, e.g. 0.015%, are also deleterious.

Two types of treatment produce significant improvement in the weldability of cast Monel: (i) addition of niobium,<sup>6</sup> (ii) treatment of the molten alloy with gaseous oxygen. The results of adding niobium are illustrated in Figs. 15 (b) and (c) (Plate LI), from which it is clear that satisfactory weldability is achieved at a niobium content of 2%. An example of a weld in Monel made from oxygen-treated pig is given in Fig. 15 (d) (Plate LI).

### IV.—CASTING PROPERTIES

The casting properties of the alloys (with the exception of Graphitic Nickel) have been shown<sup>7</sup> to be as indicated in Figs. 9 and 10. In the nomenclature used, "fluidity" is defined as the length of casting run in a standard spiral mould, and "casting quality" is the

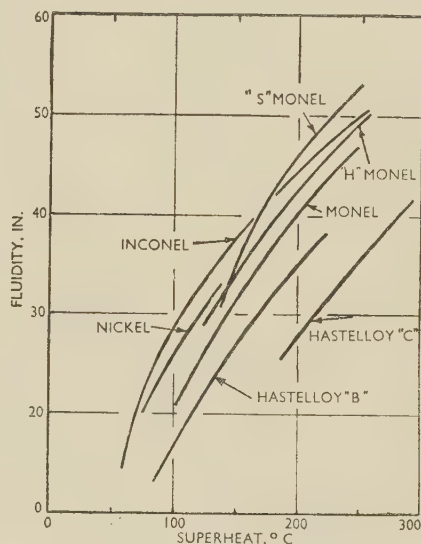


Fig. 9.—The Effects of Superheat on the Fluidity of Various Nickel-Base Casting Alloys.

percentage of the spiral casting which has reproduced the mould contour satisfactorily. An alloy having good castability is one which, in the given test, shows adequate fluidity and casting quality over a reasonable range of pouring temperatures.

From the standpoint of casting quality, the alloys fall into three groups: (1) those showing high casting quality over a wide range of pouring temperatures, e.g. Monel, "S" Monel, "H" Monel, and Hastelloy "B"; (2) those having limited casting quality at low pouring temperatures, but showing a steep increase in casting quality with increasing pouring temperature, e.g. Nickel; and (3) those having low casting quality at all practical amounts of superheat, e.g. Inconel and Hastelloy "C". It follows that alloys in group (1) will readily give castings showing good reproduction of mould contour, group (2) will be satisfactory at sufficiently high pouring temperatures, while group (3) will not be expected to give good castings in complicated moulds at any practical pouring temperature.

It has been shown<sup>7</sup> that the casting quality of Inconel, an alloy having relatively poor castability, can be im-

proved by increasing the silicon content. For example, increasing the silicon content of Inconel from 1 to 2% doubles the casting quality, and a further increase in the silicon content to 3% again doubles it, giving values greater than 90% over the pouring-temperature range 1430°–1590° C. (i.e. superheat 80°–240° C.). For normal

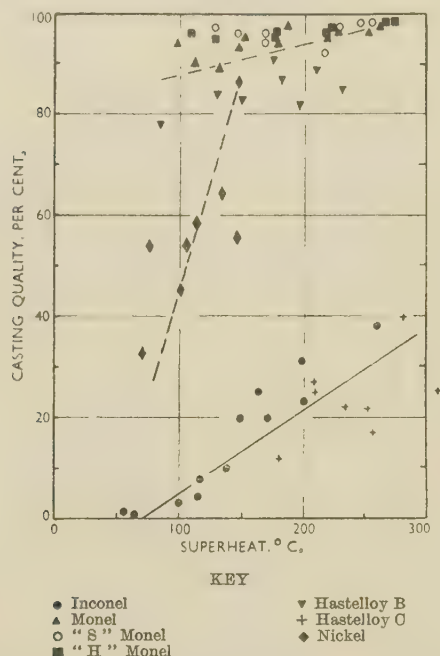


FIG. 10.—The Effects of Superheat on the Casting Quality of Various Nickel-Base Casting Alloys.

applications, however, the limit of silicon content is set at 2.0%, to avoid detriment to the mechanical and corrosion-resisting properties of the alloy.

## V.—MELTING PROCEDURES

In melting nickel alloys, a great many variations are possible in the procedure for making a given casting satisfactorily. The present description will, therefore, be confined to factors upon which good melting practice depends.

### 1. GENERAL PRINCIPLES

The basic principles underlying the melting and casting of nickel-base alloys are, in general, similar to those of steel founding, and it is therefore desirable to use the furnace refractories, melting procedures, and moulding techniques appropriate to steel, rather than those normally employed for copper- or aluminium-base alloys. The furnaces used must be capable of melting the charge of metal in a reasonably short time, and giving pouring temperatures in the range 1450°–1600° C.

Solubility relationships between carbon, which is present as an essential constituent in most of the nickel alloys, and oxygen are similar to those in steel, and to avoid producing oxidized metal, which is mechanically weak and brittle, deoxidation is carried out by silicon and similar additions.

Porosity due to hydrogen can occur in all the nickel

alloys, and nitrogen has a similar effect in the alloys containing chromium. Methods of control are threefold, viz. to minimize the gas content of the molten alloy, to add small amounts of elements having sufficient affinity for these gases to prevent their release on cooling and solidification, and to avoid introducing gas during casting.

Time and temperature are two major factors affecting reactions occurring during melting, and control of quality during melting is dependent on strict control of these variables. In general, high melt temperatures should be avoided, except for achieving specific results, for example, oxidation by gaseous oxygen, the guiding principle being that reaction with the gaseous environment is enhanced by raising the temperature of the melt. For example, an increase in temperature of 100° C. will approximately double the oxygen solubility.

The above reactions are also affected by the time factor. In general, each stage of the melting cycle, from charging to pouring, should be accomplished in the shortest possible time, unless some specific objective, such as removal of sulphur by slag treatment, has to be achieved.

### 2. RAW MATERIALS

The raw materials, other than returned scrap, normally used for manufacturing nickel alloy castings are listed in Table V, together with some details of their general composition and impurity contents.

When these raw materials form the charge for nickel-base alloys, there is no risk of contamination with sulphur or lead, since materials having relatively high contents of these elements are used only in small proportions. It is noteworthy, however, that some commercial carbon, particularly carbon for furnace bricks, contains up to 2% sulphur. Such a material would be unsuitable for use in producing high-carbon, nickel alloys, such as Graphitic Nickel.

In order to achieve the low impurity contents specified in Table I, contamination from furnace refractories and returned scrap must also be avoided.

The only harmful impurities likely to be introduced from the raw materials, hydrogen and nitrogen, are comparatively easily controlled during the melting operation, though wide variations in gas content, from batch to batch of raw material, tend to interfere with the smooth operation of a settled melting procedure.

Silicon and ferro-chromium, which often have high hydrogen contents, tend to increase the gas content of the heat. The hydrogen content of these materials can be reduced, however, by heat-treating for, say, 4 hr. at 600° C.

### 3. MELTING FURNACES

Coreless induction and direct-arc furnaces are widely employed for melting nickel alloys for sand castings. In these furnaces acid linings are often used, but linings based on magnesia are the most generally satisfactory. Acid linings have the advantage of cheapness, ease of installation, and resistance to thermal shock, but basic linings are to be favoured for nickel alloys because of their intrinsic capacity to remove sulphur, and their stability towards fluid basic slags which may be necessary to assist in desulphurization. It is also possible in basic linings to use high melting and pouring temperatures without risk of serious contamination of the melt.



TABLE V.—Typical Compositions of Raw Materials for Production of Nickel Alloy Sand Castings.

Material			Composition, %									
			C	Si	Fe	Cu	Other Elements				S	Pb
Nickel	Pellet		0.04	...	0.01	0.01	...	...	...	...	0.001	N.D.
	Cathode		0.005	0.01	0.01	0.04	...	...	...	...	0.001	N.D.
Chromium	Low-carbon ferro-chromium		0.04	0.03	30	<0.1	Cr 69	Ni 0.4	Mn 0.2	P 0.005	0.010	N.D.
	High-carbon ferro-chromium		5.5	1.5	25	...	Cr 67	...	...	...	0.007	N.D.
Molybdenum	Ferro-molybdenum		0.08	0.2	28	...	Mo 70	...	...	...	...	0.003
	Thermit molybdenum		0.04	0.15	0.4	0.03	Mo 98	Al 0.6	...	...	<0.01	0.0002
	Scrap wire		...	0.04	...	0.04	Mo >99	...	...	...	...	0.001
Tungsten	Ferro-tungsten		0.04	1.0	16	...	W 82	...	...	...	...	0.01
	Scrap wire		...	...	...	...	W 98	...	...	...	...	N.D.
Carbon	Graphite	Petroleum coke *	93	...	...	...	Ash 7	...	...	...	0.2	N.D.
		Electrode	95	...	...	...	Ash 5	...	...	...	0.5	0.01
Nickel-copper alloy	Monel pig	Oxidized	0.01	<0.03	1.8	30-31	Mn 0.1	Mg <0.03	Cr <0.02	...	...	...
		Deoxidized	0.04	<0.03	1.8	30-31	Mn 0.6	Mg 0.03	Cr 0.03	...	...	...
Silicon	80% Ferro-silicon		...	75-80	20	...	Al 0.5	Ti 0.1	P 0.03	...	...	N.D.
	“ Pure ” silicon		...	98	1	...	...	...	...	...	...	N.D.
Manganese	Ferro-manganese		6.5	...	17	...	Mn 75	...	...	...	...	...
	“ Pure ” manganese		<0.1	...	...	...	Mn 97	...	...	...	...	0.005

\* Partially graphitized.

N.D. = Not detected spectrographically.

Commercial basic lining mixtures often contain boron compounds, and some boron inevitably enters the melt; the degree of contamination is not, however, normally sufficient to be deleterious.

In general, small arc furnaces are most conveniently heated by the indirect process, whereas direct arc heating is favoured for larger furnaces; the borderline lies at approximately 500 lb. furnace capacity. Special melting procedures, for example, those involving the use of basic slags or oxygen lancing, are best carried out in furnaces of relatively large capacity. Small furnaces are normally used only for simple remelting operations.

In arc-furnace melting it is desirable to minimize contamination of the melt with gases by operating with short arcs, which are associated with relatively low arc voltages, particularly during the melting-down period. This practice has the additional advantages of reducing

wear on the furnace hearth and roof, and localizing the heating to the metal and slag.

It is also possible for the melt to become accidentally contaminated with carbon from the electrodes. The risk of pieces of electrode breaking off during the early stages of melting, owing to impact with pieces of bulky scrap, can be reduced by exercise of care on the part of the operator, and contamination during the later stages is at a minimum if the arc voltage is low and the slag is oxidizing or neutral.

A small and decreasing proportion of the nickel alloy sand castings produced is melted in plumbago crucibles, in coke-, gas-, or oil-fired furnaces, and under these conditions an additional source of contamination arises from access of sulphur-containing products of combustion. Serious contamination from sulphur is avoided by using a fuel of consistently low sulphur content, say less than

0.5%, by keeping the melting time short, and by maintaining an oxidizing flame.

#### 4. VIRGIN-METAL CHARGES

In melting pure nickel or nickel-30% copper alloy, gas will inevitably be picked up during the melting operation, and it is usually preferable to ensure that melting is effected under oxidizing conditions. Hydrogen can sometimes be removed merely by the introduction of excess oxygen; when this procedure is used, excess oxygen is subsequently removed by deoxidation.

It is often necessary, however, to "boil" the molten metal, and for this purpose an excess of both carbon and oxygen is provided; the evolution of carbon monoxide from the molten metal has a degassing action. In view of the importance of degassing by boiling, a detailed description of this operation is now given.

Various techniques are available for promoting a boiling action in the molten alloy, for example, in a virgin-metal charge, crushed graphite (0.1%) and black nickel oxide (0.5%) are mixed together and added to the furnace charge. Some localized boiling occurs as the charge melts down, and there is further boiling after the charge is fully molten. Alternatively, nickel oxide is melted with the solid nickel, or is added when the bath is fully melted, and carbon is introduced in the form of a graphite rod. Either process gives satisfactory results, but the latter, while requiring closer technical control, is more flexible, and therefore of greater use when conditions vary from heat to heat, owing, for example, to variations in furnace charges. When a graphite rod is used, the severity of boiling can be closely controlled by the operator, and it is possible to stop the reaction when the boiling action becomes quiescent. At this stage equilibrium will be shifting towards low oxygen, high carbon, and further treatment would lead to decreased boiling, an increase in carbon content, but no further reduction of oxygen content. This phase of the reaction, which can readily be detected by an experienced operator, corresponds to a carbon content of approximately 0.03% and an oxygen content of approximately 0.05%.

At this stage all opportunity for further boiling is removed by preliminary deoxidation. Silicon is usually employed for this purpose; the precise addition of silicon cannot be specified, owing to appreciable variations in the final stage of the carbon/oxygen reaction, but boiling ceases when the silicon content of the melt reaches approximately 0.2%. The corresponding oxygen content is of the order of 0.01%. In practice, a residual silicon content of 0.2% usually results from an addition of 0.3–0.4% silicon.

Carbon is then added in the form of graphite, which usually gives a melting recovery of 70–90% when the graphite is thoroughly stirred in and given adequate time to dissolve.

Alloying additions of silicon and manganese are introduced, to bring the contents of these elements to the desired levels, and, when necessary, further alloy additions are then made, sufficient time being allowed for complete solution.

Carbon may be added to chromium-containing alloys as high-carbon ferro-chromium, giving a high and consistent yield of carbon.

The solubility of nitrogen in nickel-chromium alloys increases significantly with temperature, and there is evidence that a molten nickel-chromium alloy rapidly absorbs nitrogen from the atmosphere. In heats based on virgin-metal charges, therefore, the equilibrium nitrogen content will be quickly reached, regardless of earlier degassing of the nickel or a low nitrogen content in the ferro-chromium. Under favourable conditions, viz. quick melting, low nitrogen in the ferro-chromium, and possibly the use of a slag cover, absorption of nitrogen can be restrained somewhat. Otherwise, sufficient nitrogen may be absorbed to promote gas porosity in the castings, owing to rejection of nitrogen during cooling and solidification. In these circumstances, additions of 0.1–0.2% titanium or zirconium should be made to the melt immediately before pouring.

#### 5. DEOXIDATION AND DESULPHURIZATION

Final deoxidation is effected by plunging magnesium or calcium silicide into the molten alloy, either in the furnace or in the ladle, giving an effective oxygen content appreciably below 0.01%. In nickel-base alloys, calcium and magnesium are used as deoxidants; in addition, these elements eliminate the harmful effects of sulphur. In each case the practical effect is the same, but the modes of operation are different. Calcium, if brought into intimate contact with molten nickel alloy, will remove sulphur as calcium sulphide, which floats to the surface and can be removed as a slag. Magnesium forms a sulphide which is probably soluble in liquid nickel. Magnesium sulphide is retained in the casting, but is an innocuous constituent of the microstructure. As a general rule, the residual magnesium content in Nickel and Monel should be not less than twice the sulphur content. To achieve a residual content of 0.10%, the addition of magnesium would normally be approximately 0.13%.

When calcium is used, the addition is 0.05–0.10%, in the form of calcium-silicon alloy containing 30% calcium. Some desulphurization is effected by plunging the calcium addition into the melt and skimming off the slag formed, but more complete desulphurization is achieved by adding calcium through a fluid basic slag, which is subsequently removed from the melt. A suitable slag would contain 63% "dead-burned" lime, 30% sodium silicate, and 7% cryolite or sodium silicofluoride (lead-free). Typical analysis figures for a heat of Inconel treated with calcium and a slag are as follows:

		Chemical Composition	
		S, %	Ca, %
Before treatment	.	0.006	0.005
After treatment	.	0.003	0.016

It has been reported in the literature<sup>8</sup> that additions of approximately 0.005% lithium, made to Monel after deoxidation with 0.08% magnesium, result in useful improvements in tensile properties and freedom from finely distributed shrinkage porosity.

Desulphurization can be carried out merely by application of a fluid basic slag, but the time necessary for treatment is somewhat long, and this technique is normally used only to lower very high sulphur contents, for example, to desulphurize a badly contaminated batch of scrap containing, say, 0.2% sulphur. Basic slags are employed most efficiently in direct-arc furnaces, owing



to the fact that the slag is kept very hot, but they can usefully be applied in high-frequency induction furnaces provided that the slag is frequently rabbled with a bar.

## 6. MELTING GRAPHITIC NICKEL

Graphitic Nickel is melted according to the broad principles laid down earlier, and is most readily made in high-frequency induction or electric-arc furnaces.<sup>2</sup>

After melting the nickel, degassing, and initially deoxidizing with silicon, approximately 2% carbon (preferably in the form of crushed, ungraphitized electrode carbon) is charged on to the surface of the melt, which is held for a considerable period at a high temperature. A suitable treatment would be 20 min. at 1580°–1600° C.

When subsequent alloying additions of silicon, tin, &c., are made, some carbon is thrown out of solution, and further treatment at similar temperatures is necessary to allow it to redissolve. A final carbon content of 1.5% can, however, be achieved without difficulty.

## 7. SCRAP-METAL CHARGES

A large proportion of nickel alloy heats are based on charges containing high percentages of returned scrap. In the interests of maximum quality, the ideal melting procedure would be one in which all returned scrap was melted down, oxygen lanced, deoxidized, cast as pig, and analysed before being used to make castings. In practice such a procedure is not always necessary, but high quality is achieved only if close control is maintained over (a) gas content and (b) chemical composition, with particular reference to trace elements, as previously described. Heavy scrap is clearly a highly satisfactory ingredient, because of its known composition, speed of melting, and small surface area, giving minimum carry-over of dirt, oil, &c., and minimum sorption of gas during melting. Light scrap is more difficult to handle, and in foundries which are called upon to include in their furnace charges substantial proportions of machining scrap, close attention should be paid to washing, drying, and baling such material.

Assuming a supply of satisfactory scrap, the melting procedure for chromium-free alloys is similar to that described for virgin metals. In these alloys, excessive gas content is less frequently encountered than in virgin-metal charges, owing to the low gas content of good scrap compared with that of virgin metals, and the shorter melting time required.

Difficulty in boiling scrap-metal charges arises from the substantial proportions of deoxidizing elements, for example, silicon and manganese, present in the scrap, which require correspondingly larger additions of oxygen, with the resulting need to remove large quantities of oxides from the melt.

Subject to these limitations, however, Nickel and Monel can be boiled satisfactorily. A limited boiling action can be produced in nickel-molybdenum alloys, but none is possible in nickel-chromium alloys, without resorting to high melt temperatures or to oxygen lancing.

Final deoxidation for scrap-metal charges is similar to that used for virgin-metal heats.

In the chromium-containing alloys, the tendency to pick up nitrogen during melting may be less pronounced

than with virgin metals, owing to the shorter melting time, but, where necessary, titanium or zirconium is added, as described above.

## 8. OXYGEN TREATMENT

Oxygen treatment has the general advantage of eliminating hydrogen and most of the other minor elements, and its use is to be encouraged as a means of achieving and maintaining a high level of metal quality in foundries, where repeated remelting of scrap is likely to lead to progressive build-up of tramp elements. An additional advantage is that oxygen treatment provides a raw material of standard composition, which can be readily alloyed to give closely controlled contents of such elements as carbon and silicon. Oxygen-lanced Monel is, furthermore, suitable for making weldable castings.

Oxygen lancing is most readily carried out in large direct-arc furnaces, but satisfactory results can be obtained in small arc furnaces or in high-frequency furnaces.

In arc-furnace practice, a stream of oxygen gas is passed through a refractory-coated,  $\frac{1}{2}$ -in.-dia. tube, just below the surface of the molten alloy. In high-frequency furnace practice, the oxygen gas is directed on to the surface. If large amounts of carbon, silicon, &c., have to be removed from Nickel or Monel, the reaction is exothermic, and no additional heat is usually required to maintain a given bath temperature. Nickel and Monel are most satisfactorily lanced at approximately 1580° and 1520° C., respectively. Chromium-containing alloys of the Inconel type are best lanced at approximately 1600° C., in order to minimize oxidation of chromium. Such chromium oxide as is produced can be reduced by making small additions of a suitable reducing agent, for example calcium silicide, to the slag, after lancing.

An example of the advantage to be gained from oxygen lancing is provided by cast Inconel. From the chemical compositions given in Table VI it will be observed that oxygen lancing has not served to eliminate all the minor elements (titanium, magnesium, &c.) present in the wrought scrap, the only changes in the contents of minor elements being small reductions in aluminium, boron, and lead. Castings made from scrap and treated with gaseous oxygen have, however, shown pronounced improvement in ultimate tensile strength, ductility, and impact strength (Table VI); the properties so obtained closely approach those of heats made from virgin metals. These data illustrate the use of oxygen lancing in securing, from scrap material of unknown or doubtful quality, the properties of heats made under the most favourable conditions from the best available virgin metals.

Analytical data showing the effects of oxygen lancing on the chemical composition of Monel melted in two types of electric furnace are given in Table VII. It will be noted that in both types of furnace phosphorus, silicon, manganese, and chromium contents have been significantly reduced, but that sulphur has been unaffected. In the arc furnace, lead also was reduced by oxygen lancing.

The data given in Table VIII show the high level of mechanical properties which can be obtained from Monel castings made either direct from oxygen-lanced metal, or by remelting pig cast from oxygen-lanced metal. It has been found satisfactory to lance gaseous oxygen into

TABLE VI.—Chemical Compositions and Mechanical Properties of Cast Inconel Containing 3% Silicon, Made from (a) Untreated Inconel Scrap, (b) Oxygen-Lanced Inconel Scrap and (c) Virgin Metals.

Basis of Charge	Composition, %											U.T.S., tons/ in. <sup>2</sup>	Elonga- tion, % on 2 in.	Izod Impact Value, ft.-lb.
	C	Si	Mn	Fe	Cr	Ti	Al	Mg	B	Pb	Ni			
(a) Inconel Scrap . . .	0.07	3.2	1.25	7.1	14.5	0.01	0.04	0.01	0.03	0.008	Bal.	33.2	15.5	45
(b) Oxidized Inconel Scrap *	0.05	3.15	1.15	7.5	13.8	0.01	0.03	0.01	0.02	0.006	„	37.1	29.5	89
(c) Virgin Metals . . .	0.04	3.0	1.05	6.5	13.7	N.D.	N.D.	N.D.	N.D.	N.D.	„	38.3	35.3	102

\* Made by oxygen lancing Inconel scrap (a), and treated with additions of low-carbon ferro-chromium (0.22% chromium), 0.10% calcium (as calcium silicide), silicon, and manganese.

N.D. = Not determined.

TABLE VII.—Oxidation of Molten Monel by Gaseous Oxygen.

Type of Heat	Oxygen Treat- ment	Composition, %										
		C	S	P	Cu	Si	Fe	Mn	Cr	Mg	Pb	Ni
5-Cwt. H.F. Furnace	Before	0.08	0.012	0.028	31.0	0.07	1.37	0.73	0.05	Trace	...	Bal.
	After	0.01	0.013	0.010	29.2	0.01	1.56	0.19	Trace	„	...	„
40-Cwt. Direct- Arc Furnace	Before	0.10	0.009	0.025	31.2	0.06	1.5	0.75	0.03	Trace	0.008	Bal.
	After	0.006	0.011	0.006	31.2	0.006	1.4	0.10	Trace	„	<0.005	„

the molten alloy in such a way as to oxidize the carbon and silicon contents to low levels, viz. less than 0.02 and 0.03%, respectively.

TABLE VIII.—Mechanical Properties of Monel Castings Made from Oxidized Raw Materials.

Melting Procedure (Induction Furnace)	U.T.S., tons/in. <sup>2</sup>	Elonga- tion, % on 2 in.	Izod Impact Strength, ft.-lb.
Monel scrap, treated with oxygen, deoxidized, poured as sand castings . . .	35.0	43	89
Monel scrap, treated with oxygen, cast as pig. Re- melted, deoxidized, poured as sand castings . . .	36.0	48	91

opportunity must be given for unhindered contraction of the solid alloy.

High-quality castings, for example castings for pressure-tight applications, are cast in dry-sand moulds, made from washed silica sands, graded to give high permeability, and bonded to secure the following properties:

Permeability, A.F.A. No. . . .	Above 80
Green compression strength . . .	4-5 lb./in. <sup>2</sup>
Dry compression strength . . .	approx. 50 lb./in. <sup>2</sup>
Gas evolution on heating . . .	Very low

For less exacting purposes, for which green-sand practice is satisfactory, a facing sand of the following composition may be used:

	%
Fine silica sand (washed) . . .	58
Coarse silica sand (washed) . . .	30
Coal dust . . .	3.5
Bentonite . . .	3.0
Core gum . . .	0.5
Water . . .	5.0

## VI.—MOULDING AND CASTING

Nickel alloys show high liquid shrinkage compared with, say, cast iron or gun-metal, and casting designs which are satisfactory for the latter alloys rarely produce high-quality sand castings in nickel-base materials. In designing the runner and riser systems, the established principles of directional solidification, associated with provision of adequate risers, are applied, and in view of the high melting points of nickel alloys and their consequent readiness to freeze over rapidly, insulating or exothermic feeder sleeves are often used to advantage. Choke gates are usually preferred. An example of running and feeding techniques used successfully for Monel is given in Fig. 16 (Plate LII).

Adequate allowance must be made for the solid contraction, which for practical purposes may be taken as  $\frac{1}{4}$  in./ft., and in large and complicated castings every

Readily collapsible cores are essential, particularly with Nickel and Monel, in view of the low strength of these metals at temperatures immediately below the solidus, combined with their relatively high shrinkage. A low evolution of gas is secured by using a washed silica sand bonded with linseed oil, and the need for rapid escape of gas, from both mould and core, is met by extensive venting. Cores made by the "CO<sub>2</sub>" process are satisfactory.

Mould dressings are as varied with nickel alloys as with other foundry alloys. A generally acceptable coating consists of dry, powdered plumbago, rubbed on to the mould surface, or a fine refractory sand such as silica or zircon flour, which can, for example, be applied as an aqueous suspension.



The high permeability of shell moulds makes them attractive for nickel alloys, and Monel castings have been made successfully in such moulds. There is some evidence, however, that the refractoriness of silica-sand shell moulds is less than that of a high-grade, silica facing sand, and care must therefore be taken to avoid excessive pouring temperatures when casting into shell moulds.

Pouring temperatures, which must be accurately controlled, are most satisfactorily measured by means of a quick-response immersion thermocouple. For this purpose, a platinum/platinum-rhodium thermocouple, protected by a thin-walled silica sheath, is usually employed, connected to a D.C. amplifier and giving a reading on a large dial or a recorder. Optical pyrometers can be used successfully for molten nickel alloys only when melting and pouring conditions remain unaltered for long runs of successive heats.

A guide to optimum pouring temperatures for high-nickel alloys is given in Table I (p. 320).

## VII.—INSPECTION: TEST-BARS

Finished nickel alloy castings are inspected and released for sale according to individual contract, but the procedures normally adopted may include general inspection, test-bar data, pressure testing (non-destructive), and proof testing (destructive).

General examination of nickel alloy castings is similar to that applied to other castings: X-ray examination, ultrasonic testing, and the use of dye penetrants supplement visual examination.

The practice of using "cast-on" test-bars, formerly widespread, has now been largely superseded by separately cast samples. In the design of these bars an important requirement is adequate feeding, but freedom from oxide films and entrapped dross is also essential. Keel-type bars, illustrated in Fig. 11, meet these requirements satisfactorily.

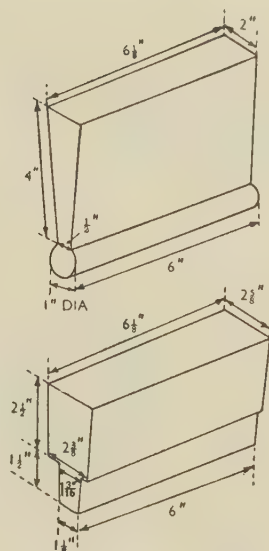


FIG. 11.—Keel-Type Test-Bar Castings.

## ACKNOWLEDGEMENT

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# 1752 THE CONTROL OF QUALITY OF PRESSURE DIE-CASTINGS\*

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## SYNOPSIS

Measures that can be taken during the production of pressure die-castings to ensure the attainment of a high standard of quality are discussed. The aspects covered include selection of suitable machines, alloys for pressure die-casting, detection and elimination of defects, control of metal quality, casting and die design, the maintenance of a suitable heat balance in the die cavity, control of metal flow into the die, and the effects of injection pressure. The interaction of these variables with one another is considered.

At all stages close liaison between the Inspection and Production Departments is recommended to ensure that deviations from the established standard of quality are immediately detected and corrective measures applied.

## I.—INTRODUCTION

PRESSURE die-casting differs radically from other casting processes in several important respects. By using extremely high injection pressures to force the liquid metal into the water-cooled metal die cavity, very good thermal contact is achieved and an intense chilling action results. Rapid filling of the cavity therefore becomes essential, and special consideration must be given to the venting of the cavity.

A feature of the process is the large number of inter-related variables, and while, for any given casting, certain conditions become fixed once the design of die and casting have been decided upon, a considerable amount of variation may still occur in the casting process itself.

In the case of simple castings, particularly in the zinc-base alloys, it is possible to institute sufficient controls to render fully automatic casting a practical proposition. The majority of pressure die-castings, however, are produced under conditions which may be described as semi-automatic. The human factor then becomes an essential part of the process, and the casting conditions—and consequently the quality of the products—are dependent on the skill of the operator in conjunction with the correct regulation and setting of the controls of the die-casting machine.

## II.—PRESSURE DIE-CASTING MACHINES

The various types of die-casting machine differ mainly in the method of applying the injection pressure. Three main types are in use at present. In one of these, the metal to be cast is held in a closed crucible provided with a submerged outlet like that of a kettle. Air pressure exerted above the surface of the molten alloy forces it directly into the die. This is the "air-operated goose-neck machine". In a second type, the "piston-operated goose-neck machine", displacement is effected by means of an air-operated, submerged piston and cylinder. Both these are "hot-chamber machines", the metal being completely fluid until it

enters the die. Relatively low injection pressures are used, of the order of 500 lb./in.<sup>2</sup>, the pressure being applied almost solely to obtain sufficient injection speed to fill the die cavity before chilling of the molten alloy occurs.

In the third type, the molten alloy is ladled from a holding furnace into an injection cylinder, and then

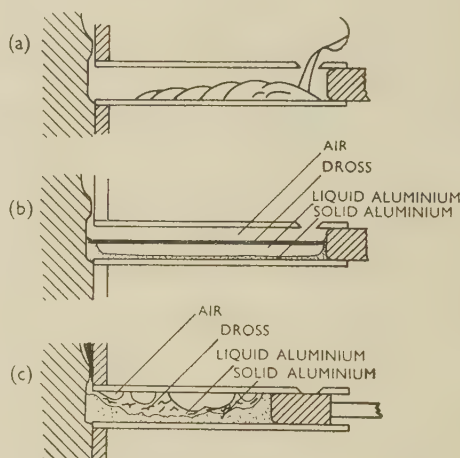


FIG. 1.—Cold-Chamber Pressure Die-Casting Machine of the Horizontal-Sleeve Type. Stages (a)–(c) show that considerable chilling of the metal takes place before injection.

forced into the die by means of a piston. This forms the basic principle of the cold-chamber machine. Relatively high pressures are necessary, largely because of the chilling action of the injection sleeve on the metal being cast. This is illustrated in Fig. 1. The degree of chilling is sometimes so great that the first metal injected may be in the solid state. In such cases, extrusion of the solid material through the gate takes place, the frictional heat developed being sufficient to convert the material back to the liquid state as it enters the die. This condition is typical of the cold-chamber machine having a horizontally

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disposed injection sleeve, and has been largely responsible for the trend towards higher and higher injection pressures. This, in its turn, has necessitated higher and higher clamping pressures and more robust machine frames to withstand the resulting stresses. In contrast, the vertical injection sleeve, which is typical of Continental practice, gives far less chilling of the metal, and lower injection pressures can generally be used. A comparison of Figs. 1 and 2 illustrates this point. Such machines are usually of much lighter construction.

These fundamental differences in design must be borne in mind if full advantage is to be taken of the merits of a particular type of machine. For example, the piston-operated goose-neck machine is ideal for castings in zinc-base alloys, as high operating speeds can be maintained. For brass die-casting, however, a vertical-injection cold-chamber machine is invariably used, as this gives the

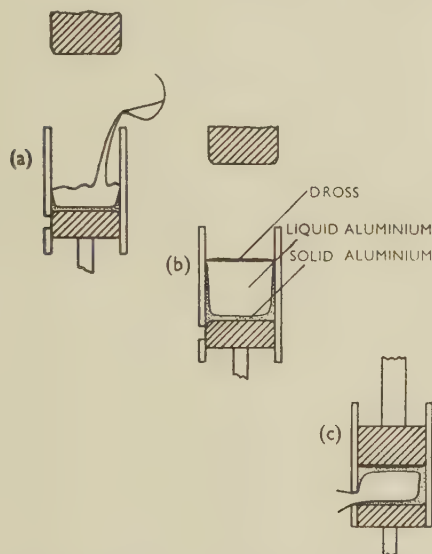


FIG. 2.—Cold-Chamber Pressure Die-Casting Machine of the Vertical-Sleeve Type. Comparison of stages (a)–(c) with Fig. 1 shows that far less chilling occurs and that no air is injected into the metal.

minimum of chilling. Similarly, magnesium alloys, which have a low heat content, need high injection speeds with a minimum of chilling before injection. They are therefore more successfully cast with a vertical rather than a horizontal injection sleeve. The ideal machine for magnesium is a piston-operated goose-neck type, and very large magnesium castings are now being successfully produced on such machines. The technique was largely developed by Mahle K.G. of Stuttgart during the war. A high proportion of the magnesium castings produced at that time in Germany were made by this method, and it is still being very successfully applied. Further developments of this basic principle have recently been brought to the stage of a production process by the Dow Chemical Company.\*

In the case of aluminium alloys, particularly when heavy sections have to be cast with a high degree of soundness, a horizontal-injection cold-chamber machine is preferred, capable of exerting a very high injection pressure. The technique is then to use the maximum

injection pressure to force the semi-molten alloy through a large gate at a relatively slow speed.

### III.—MAIN TYPES OF DEFECT

The main defects found in pressure die-castings arise from the necessity of forcing the liquid metal into the cavity at very high speed in order to fill it completely before solidification occurs, and at the same time to provide adequate means for the escape of the air which is being displaced. As the time of filling the cavity is reduced, the defects due to misruns and cold shuts become fewer. At the same time it becomes more difficult with rapid filling to vent the cavity adequately, and the entrapped air causes porosity and blow-holes.

In addition to these two main types of defect, several other types are found on occasion. If flow rates through the gate are excessively high, the turbulence produced results in severe surface flow-marks. A combination of heavy and light sections in one casting can lead to heat sinks, owing to solidification shrinkage in the heavier section. Hot tearing, due to contraction on to the male portion of the die before ejection, is liable to occur with excessive dwell times. Magnesium alloys are more prone to this effect than aluminium alloys. Distortion of the casting while being ejected from the die may take place, and in the case of castings being produced to very close dimensional tolerances, variations in die temperature may be sufficient to produce castings outside the dimensional limits. Finally, the excessive or incorrect use of die lubricants may produce surface blemishes.

With the exception of porosity and blow-holes due to entrapped air, all the defects mentioned above are apparent on visual inspection. Blow-holes and internal porosity cannot, of course, be detected in this way, and recourse has to be made to radiography or some form of destructive testing. It is not usual to give pressure die-castings a 100% X-ray examination, but rather to pay adequate attention to the initial design of casting and die in order to eliminate as far as possible the conditions liable to lead to defects. The systematic X-ray examination of castings during the initial operation of the die may then be used to determine the optimum die-operating conditions for the production of sound castings. The weight of the casting is sometimes used as a check on soundness. This method has not been found to be a very reliable one, however, as small dimensional changes, due to the split line and die temperature, are often enough to mask weight changes due to entrapped air.

### IV.—ALLOYS FOR PRESSURE DIE-CASTING

#### 1. METAL QUALITY

The majority of pressure die-castings are produced in either zinc-base or aluminium-base alloys. A small tonnage of magnesium alloy castings is also being produced and some brass castings are being made.

In the author's opinion, far too much time is devoted to checking raw materials to ensure that they comply in composition with specifications, without a proper assessment having been made of just how important the composition limits specified are. This is particularly the case with aluminium alloys. Similarly, far too much

\* This advanced process for magnesium is covered by British Patent No. 731,038.

emphasis is placed on mechanical properties. The general run of pressure die-castings, at least, merely form a base to which are attached many other components, and provided that there is sufficient metal at the right places to form the various flanges and bosses required for drilling and tapping, the casting as a whole will almost certainly have more than adequate strength for its purpose, even if its composition happens to fall well outside the specified limits.

In the case of pressure die-castings, it is important to control the composition of the metal being cast only in so far as this affects castability, machinability, sometimes corrosion-resistance, and, occasionally, physical properties. It should be noted that castability and machinability are mentioned first. They vitally influence the production of the casting rather than its service life.

The most important physical property from the point of view of performance is adequate impact-resistance. In addition, for some applications, ductility is required, in order that certain forming operations may be carried out after casting.

## 2. ALUMINIUM ALLOYS

As yet, there is little reliable information about the effect of alloying elements on the castability by the pressure die-casting process of alloys of aluminium, except that greatest castability is found in the aluminium-11-12% silicon alloy. An alloy of this composition also gives castings with the highest mechanical properties and corrosion-resistance, provided that sufficient chilling occurs in the die to ensure chill modification of the alloy.

Elements such as silicon, copper, magnesium, iron, and zinc, found in the aluminium alloys commonly used for pressure die-castings, are present in widely differing proportions, some being intentionally added in large or small amounts for specific reasons, while others may be regarded essentially as impurities.

The majority of aluminium pressure die-castings are now made in alloys containing 5% or more silicon. Pressure methods can be successfully applied to casting thin sections in the aluminium-silicon eutectic alloy LM6,\* which has also excellent corrosion-resistance and mechanical properties. When heavy sections are involved, however, the lack of sufficient chill modification leads to hot sinks, as well as machining difficulties due to the presence of massive silicon. The most suitable all-round alloy is LM2,† and the majority of pressure die-castings are produced in this material. It offers very good castability over a wide range of sections, has reasonable mechanical properties and corrosion-resistance, and is cheap. Its two main defects are poor elongation and machinability. Pressure die-castings for special applications are made in other alloys, including the 10% copper alloy LM12. This is used for the sole plates of domestic irons because of its relatively high hot-hardness and scratch-resistance. The 6% magnesium alloy (LM5) is used when a casting of greater strength than LM2 is required; it may be anodized or polished to a white finish.

A great deal has been written concerning the necessity of degassing aluminium alloys before casting, but in the author's experience this does not apply to pressure die-

casting. Comparative trials conducted over a long period failed to show any advantage in degassing at any stage. Because of the manner in which the alloy is maintained in the molten condition for prolonged periods in the holding crucibles and because of the use of grease and other lubricants on the injection plunger, &c., ample opportunity for gas pick-up exists at all stages of the process. As a result of the high injection pressure and rapid chilling, however, the evolution of gas is always suppressed.

Methods available for checking the composition of the aluminium alloys and of the finished castings include spectrographic and colorimetric analysis, as well as the usual wet chemical methods. The method actually used will depend upon the extent of the testing involved. Colorimetric analysis is probably the more usual method, though spectrographic methods, besides being ideal for handling large numbers of analyses, have the advantage of producing a result in the shortest possible time.

The amount of checking for metal composition will vary according to the particular system of melting and the number of different alloys used in the foundry. It is usual to cast a very limited range of alloys, however, because, as already noted, aluminium alloys other than those of the high-silicon type in general offer no special advantage from the point of view of either production or performance, as pressure die-castings. The random checking of incoming ingots to confirm the supplier's analysis sheet, coupled with the controlled checking of remelted material, is usually sufficient to maintain adequate metal quality. The most important points to guard against are usually build-up of iron in the system and a lowering of silicon content due to the ingress of alloys less rich in silicon.

A light drossing off at the remelt stage should be provided for, but apart from this, no fluxing is used. Metal at the die-casting machine is not fluxed at all. A very simple and reliable guide to quality is the fracture of a small chill-cast ingot, as the appearance of the fracture gives an indication of ductility, grain-size, and freedom from dross.

## 3. MAGNESIUM ALLOYS

The nominal composition of the alloy used for magnesium pressure die-castings has now been stabilized at: aluminium 9, manganese 0.2, zinc 0.6%, balance magnesium. As the aluminium content is raised, fluidity increases at the expense of ductility and corrosion-resistance. At an aluminium content of 9% fluidity is good and the elongation about 2%; with 10% aluminium, elongation is reduced to 1% with no noticeable improvement in fluidity. Zinc up to 1% has no effect on the mechanical properties or castability, provided that the aluminium content is kept up to the full 9%.

One of the principal production difficulties connected with the magnesium alloys is the necessity at all times of maintaining a protective atmosphere over them when in the molten state. Sulphur dioxide gas is generally used for this purpose, in conjunction with a hooded holding pot. Sometimes 0.0001% beryllium is added with a view to reducing oxidation, although it is doubtful whether this addition is, in fact, of any practical value. A further difficulty arises from the proneness of magnesium alloys

\* The LM designations refer to British Standard No. 1490.

† Silicon 9-11.5, copper 0.7-2.5; zinc 1.2, nickel 1, iron 1% max.



to flux inclusions. During the remelting and refining stages, a suitable fluxing procedure is essential, and rigorous precautions have to be taken effectively to free the metal from this flux when casting the ingot or transferring to the holding furnace before die-casting. Contamination of the alloy with flux leads to subsequent corrosion of the castings, as well as causing welding on to the die. The best procedure is to check all melts at the ingot stage by casting a small bar with the ingot, breaking it, and leaving the broken ends exposed to the weather for a few days. If flux inclusions are present, they show up as very obvious areas of corrosion.

#### 4. ZINC ALLOYS

The intelligent application of a few simple physical tests, coupled with random chemical analysis employing either the usual wet methods or, if convenient, the spectrographic technique, is sufficient to ensure the quality of magnesium and aluminium alloys from a production and service point of view.

This is not the case, however, with the zinc-base alloys, which are subject to intercrystalline corrosion if certain impurities, i.e. lead, tin, and cadmium, are present. The level at which these impurities can be tolerated is so low that special precautions have to be taken with regard to the grade of zinc used, and subsequently to prevent contamination during casting and remelting. A further complication is that a special technique is needed to determine these impurities accurately, because of the low percentages involved. The method usually adopted is spectrographic analysis employing the Hilger medium quartz spectrograph. Although simple, once the apparatus is set up and the technique established, the method is specialized and demands constant attention to detail. Samples have to be cast and machined in a standard way, so that direct determinations cannot be carried out on the die-castings themselves. It is necessary to obtain a supply of "standards", which have been carefully cast and checked for composition by the laborious wet method of analysis.

A more direct method of quality control is the "steam testing" of representative castings. Die-cast tensile-test specimens or actual castings are exposed to water vapour at 95° C. and 1 atm. for 10 days, after which the specimens are examined for growth and mechanical properties. While this is a very simple test, it has the drawback of holding up clearance of castings pending the result. By far the best procedure is control of metal quality by spectrographic analysis of all batches of ingots, and subsequent attention to cleanliness during melting and casting.

The composition requirements of the zinc-base pressure die-casting alloys are covered in B.S. 1004. This specification includes two alloys, A and B, the composition limits for which are:

		Alloy A		Alloy B	
		%		%	
Aluminium	min.	3.9		3.9	
	max.	4.3		4.3	
Copper	min.	...		0.75	
	max.	0.03		1.25	
Magnesium	min.	0.03		0.03	
	max.	0.06		0.06	
Iron	As impurities	max.	0.075	0.075	
Lead		"	0.003	0.003	
Cadmium		"	0.003	0.003	
Tin		"	0.001	0.001	
Zinc		Remainder		Remainder	

Alloy A is that most frequently used today, having the highest dimensional stability, heat-resistance, and ductility. Alloy B is employed when a harder and stronger alloy with maximum castability is required. The aluminium content is limited to a maximum of 4.3% because above this amount the impact strength becomes adversely affected. With less than 3.9% aluminium, lower mechanical properties are obtained, and there is a falling off in castability. Magnesium is present in order to inhibit the effects of residual impurities; a minimum of 0.03% is required effectively to accomplish this. With a magnesium content above 0.05%, hot-shortness becomes evident on casting.

#### V.—DESIGN OF CASTING AND DIE

Much can be done at the early stages of designing a casting and die to ensure that a high standard of quality is subsequently maintained. It cannot be too strongly emphasized that such design considerations are essential features of positive quality control. If they are not taken into account, quality control becomes no more than an inquest after the event, to sort out the good from the bad, instead of serving its real purpose of ensuring that only good castings are produced.

All sections should be of minimum thickness consistent with reasonable ease of casting. If extra strength or stiffness is required, it should be obtained by means of suitably placed ribs and flanges. Adequate draft must also be provided. This permits the minimum use of die lubricants, thus ensuring clean, sound castings.

Once a casting has been designed to tolerate 1°–2° of draft, little is involved from a design point of view in allowing up to 4° per side, with great advantages from a production point of view. A draft of 1° per side is regarded as the minimum permissible, provided that the length of draw is under 1 in. If the draw is over 1 in. up to 3° minimum per side may be required, depending on section size and draw length. Castings can be made to tighter draft tolerances, particularly in zinc-base alloys, but casting scrap and die maintenance are increased, and this unfavourably affects the overall economics.

Not only do thinner sections require less metal, reduce machine dwell time, and ensure freedom from hot sinks and porosity, but the rapid chilling of the alloy in contact with the die walls produces a thin skin of metal that is appreciably stronger than the interior, which cools more slowly and therefore has a less favourable structure. A minimum of 0.040 in. and a maximum of 0.500 in. are generally considered as the extremes of variation in section. The minimum section from the point of view of castability is approximately related to the size of the casting.

Every possible means should be employed to ensure uniformity of section thickness throughout, but where variations are unavoidable, a gradual transition should be made. The thickest section can best be tolerated around the periphery of the casting and in the area farthest removed from the gate. When ribs are incorporated, their thickness should be 0.8–0.9 times the thickness of the adjoining section. Ribs should not be placed opposite to one another on either side of a section, but should be staggered, in order to prevent the formation of a hot spot and consequent sink.

Fillets and corner radii are essential in good design to

prevent shrinkage strains and cracks, to provide extra strength, and to distribute stresses which might tend to become localized at the junction of section and ribs, &c. Fillets also facilitate the flow of the metal, thus making it

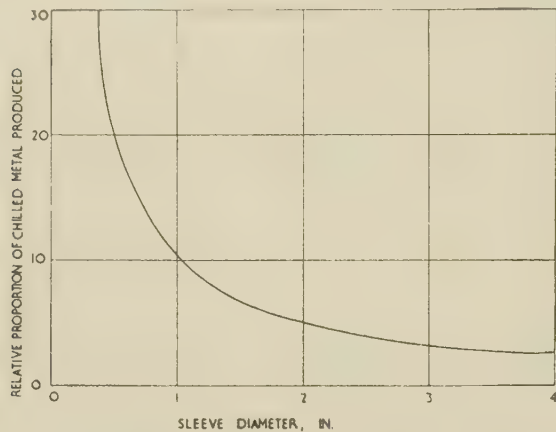


FIG. 3.—Relationship Between the Diameter of the Injection Sleeve of a Cold-Chamber Machine and the Proportion of Chilled Metal Produced.

possible to avoid turbulence and consequent porosity as the result of flowing over and around a sharp corner. As a guide to proper fillet radius, the following formula may be taken to apply to the average condition :

$$R = \frac{A + B}{3}$$

where  $R$  = radius of fillet,  $A$  = wall section, and  $B$  = adjoining wall section. Any substantial deviation from this rule will lead to : (1) cracking, due to too small a radius; or (2) shrinkage at the junction of the section and surface imperfection on a flat surface opposite the junction of the section due to too great a radius.

In considering the design of a die, attention must be paid to the suitable disposition of the gate and runner system, and also to the cavity lay-out in the case of multi-cavity dies. Sufficient cavities should be laid down in a given die to utilize the full capacity of the die-casting machine, thus achieving maximum output per man.

The following factors should also be noted as having a direct bearing on the subsequent control of casting quality when cold-chamber machines are used :

(1) The injection stroke of the machine is constant; consequently the larger the volume of metal used per shot, the larger should be the diameter of the injection sleeve. This results in the surface area : volume ratio for the sleeve being a minimum (see Fig. 3) and will ensure the least possible chilling of the metal in the sleeve before injection takes place. Moreover, the shorter the stroke of the injection ram, the better it is from the point of view of reducing metal chilling.

(2) The larger the volume of metal used per shot, the less will be the variation in temperature of the injected metal due to differences in the operator's times of ladling and pouring into the injection sleeve.

(3) The larger the sleeve diameter and the more completely it is filled by metal before injection begins, the less will be the volume of air injected into the die.

Factors (1) and (2) have a considerable influence on the occurrence of misruns and cold shuts, while factor (3) affects the amount of air entrapped in the casting.

## VI.—HEAT BALANCE IN THE DIE CAVITY

The number of cavities finally decided upon must be so disposed in the die blocks as to give a spray, which, including all necessary runners, blind runners, and overflow wells, will ensure optimum conditions for thermal balance in the die. Failure to achieve sufficient uniformity and stability in the die temperature will lead to heat sinks and cold shuts, together with poor surface finish.

It must be borne in mind that as the injected metal

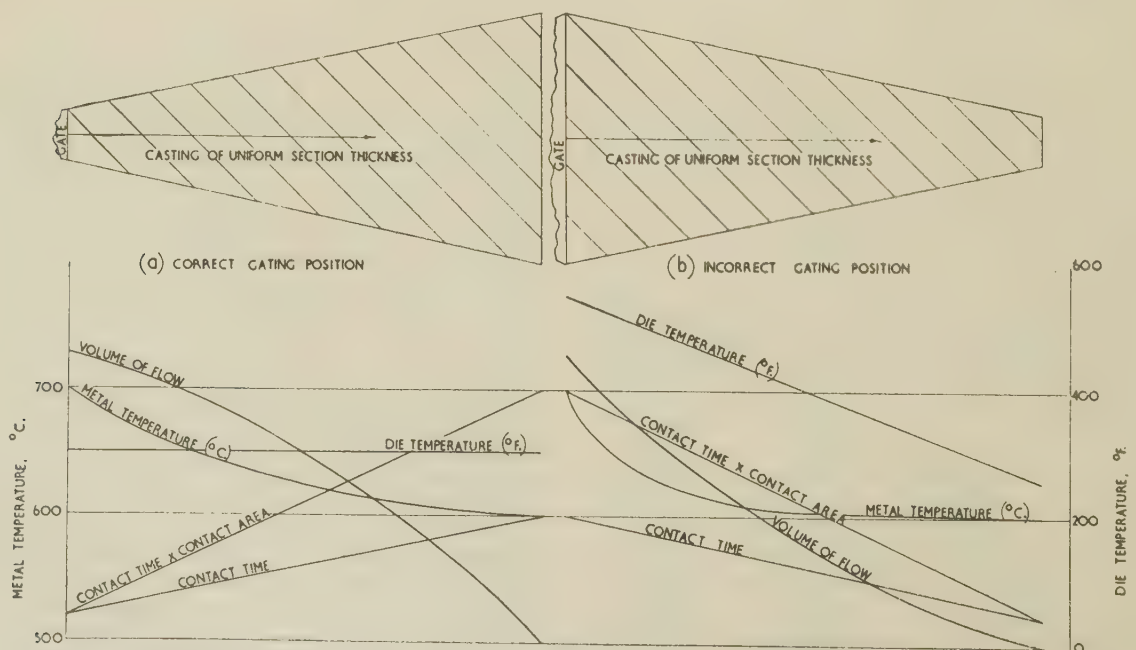


FIG. 4.—Effect of Position of Gate on Temperature Distribution in the Die. (a) Correct gating position; (b) incorrect gating position.



flows in it will lose heat to the die at a rate dependent upon: (a) the difference between its temperature and that of the die face in contact with it, (b) the area of its contact with the die, and (c) the speed of injection. As far as possible it should be arranged that the surface of the casting per unit distance from the gate increases, while the ruling section remains constant. This ensures that the hottest metal is in contact with the smallest area of the die face while as this hot metal cools on losing its heat to the die, it flows on, coming into contact with an ever larger area of die face. Although its temperature is falling and it is consequently giving up less heat per unit area per unit time, it is in contact with a larger area of die face for a longer period, thus raising the temperature of the die block by the same degree in all sections at right angles to the general direction of flow from the gate (see Fig. 4).

If heavy and light sections must be present in the same component, it is usually preferable for the heaviest sections to be remote from the gate. In order to obtain thermal balance in both single- and multiple-cavity dies, it may be necessary to resort to "back feeding", blind runners, overflow wells, &c. This will require more metal, but such a procedure is important in ensuring a consistently high quality of casting.

While the sum of such properties of the alloy being cast as heat content, thermal conductivity, and casting temperature determine the rate of heat extraction by the die, and therefore the order of injection speed required (zinc and aluminium alloys require comparable speeds, magnesium alloys much higher speeds), a more important factor is the temperature difference between the solidus and the liquidus for a given alloy. Those having the least difference, i.e. those nearest to the eutectic composition, are the easiest to cast in the usual sections. The cavity is quickly filled with liquid metal, only a small fall in temperature being then required for the whole casting to solidify. In the case of alloys having a wide freezing range, it is necessary to maintain a high pressure on them while solidification takes place, in order to try and reduce the resultant solidification shrinkage. Such alloys have some advantages, however, in the production of simple, heavy-section castings, using a large gate, a slow injection speed, and very high pressure to extrude the alloy into the cavity in a plastic state.

## VII.—METAL FLOW INTO THE CAVITY

A number of theories covering the mechanism of metal flow into the die cavity have been advanced at various times. The best known are those of (a) Frommer, which postulates filling back towards the gate; (b) Brandt, filling from the gate; (c) Köster and Jöhring, more or less a compromise between the previous two; and (d) Barton, which deals mainly with the kinetic-energy concept and resulting rise in metal temperature when the metal velocity is reduced to zero at the end of the injection stroke. None of these theories is compatible with all the facts, and in particular the first three can be applied only to simple castings. It is well established, however, that an appreciable rise in metal temperature occurs, owing to frictional heat as the metal flows through the gate. For this reason among others, the size of the gate is important in order to ensure the right balance between filling time of the cavity and energy release at

the gate. Part shots of castings will soon show the manner in which any given cavity is filled, and this serves as a useful way of assessing the position of any further venting and overflow wells required, besides indicating the necessity of modification to the form of the gate in order to obtain the optimum direction of flow. In addition to seeing that the gating is situated at the lowest point in the cross-sectional area gradient of the casting, to ensure the thermal balance of the die, an endeavour should be made to provide a smooth metal flow. It is best to avoid any conditions which favour splitting of the metal stream in the cavity, as trouble may be experienced owing to the occurrence of cold shuts when the two streams try to rejoin. For the same reason, multiple gates should not be used unless it is absolutely necessary.

In arriving at an estimate of the gate dimensions required, it has to be borne in mind that the cavity must be filled in 0.2 sec. or less, while the speed at which the metal passes through the gate should be under 3000 ft./min. (These values are calculated, using, in particular, a certain method of checking the velocity of the injection plunger. With other methods, different values are often obtained. The figures cannot as yet be considered as absolute values, but are useful for purposes of comparison.) If this speed is exceeded, turbulent flow occurs and bad formation results, especially in large flat areas of the casting. If the filling time is extended beyond 0.2 sec., trouble will be experienced from bad formation and cold shuts. A partial remedy would be to run the die at an excessively high temperature, but it is more difficult to maintain stability with a high die temperature, and satisfactory operation would never be achieved.

## VIII.—INJECTION PRESSURE

The main difference in the various cold-chamber die-casting machines, from a casting point of view, centres around the method of applying the injection pressure. This may be done by direct hydraulic action backed up by compressed nitrogen gas, by compressed nitrogen gas alone, or by means of the conventional hydraulic accumulator. Depending upon the method used, the characteristics of the injection stroke vary with respect to the pressure developed over the various phases of the stroke. The pumping arrangement will also influence the action, some machines being arranged to step the pressure up considerably at the end of the stroke.

With castings of relatively thin section, the technique is largely to fill the cavity as quickly as possible, so that the metal is in a very fluid condition and has insufficient time to become chilled in the thin sections before the whole of the cavity is filled. With this type of casting, pressure is of use only as a function of speed. There is now some evidence, although it is not at the moment conclusive, that this is most effectively accomplished with an all-hydraulic injection circuit. The reasons for this appear to be two-fold. With all-gas injection, or when there is a gas accumulator in the hydraulic circuit very near to the injection ram cylinder, slight increase in resistance, due, for example, to binding of the injection plunger in the injection sleeve, can cause relatively large fluctuations in plunger speed, particularly at the end of the stroke. With an all-hydraulic circuit, the pressure rise at the end of the stroke due to the resistance of the

filled cavity is slower than with gas/hydraulic injection. The metal can thus solidify at the split lines, &c., before the full pressure is exerted upon it; thus preventing loss of metal by splashing and metal penetration of core slides

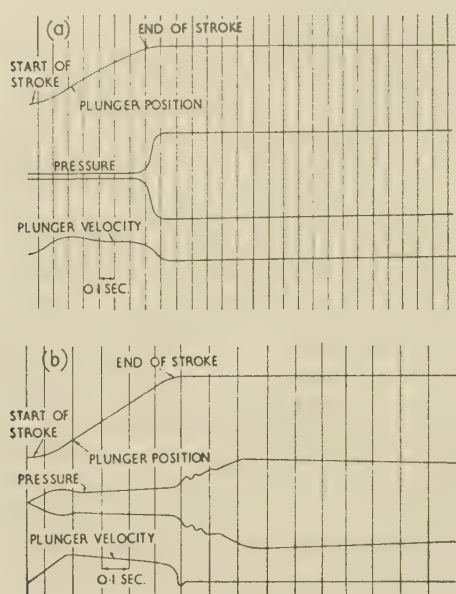


FIG. 5.—Oscillograms Showing Variation in Injection Pressure and Speed Obtained Using (a) Gas-Bottle Injection and (b) All-Hydraulic Injection.

and ejectors. It also makes it possible to use a higher injection-pressure setting and speed.

Special oscillographic equipment is required to record the injection pressure and speed with sufficient accuracy to reveal the differences attributable to different types of hydraulic circuit (see Fig. 5). With such equipment differences can be shown from shot to shot, with, in some cases, identical machine settings. Such differences are clearly sufficient to affect the quality of the castings produced. Techniques of this kind do not represent practical inspection tools, but they have proved of value in ascertaining the types of hydraulic circuit that are free from the random variations mentioned.

## IX.—PROCESS VARIABLES AND THEIR CONTROL

Because so many variables are involved in pressure die-casting, and because all these variables are to a large extent interdependent, it is most important that, having finally decided upon the casting and die, the optimum casting conditions be next ascertained by a logical approach to the die try-out. Only in this way can the consistent maintenance of a high standard of quality be achieved. The best form of approach, in the case of aluminium castings produced on cold-chamber machines, has been found to be as follows:

Arrange for a fully experienced operator to run the job during the try-out period. After the die has been warmed up and casting has begun, the injection speed should be so adjusted that the cavity is filled in between 0.1 sec. (for a large casting) and 0.05 sec. (for a small

casting). Casting should then be allowed to proceed at a regular rate suited to the job until conditions become stabilized. At first, no doubt, the castings will suffer from excessive flow marks, grease and oil stains, &c. The lubrication of the die and injection plunger should be cut down to the minimum compatible with safe operation. It will then be found that the flow marks disappear as the die warms up. A defect, however, may persist which takes the form of a flow mark but is characterized by being of a much deeper nature. This is the result of using too small a gate, which leads to excessive metal speed through the gate. The speed of flow should be under 3000 ft./min., and the gate size must be increased until this is approached. When this alteration has been made, the marks due to turbulence disappear.

Having satisfactorily established the primary variables of filling time of the cavity and velocity of metal flow through the gate, it will be found that the die temperature has adjusted itself in relation to the casting rate and the use of the water-cooling lines. The latter should be brought into operation when, as casting proceeds at a steady rate, hot sinks appear on the casting, the water flow being so regulated that the hot sinks are just prevented at the optimum casting rate.

The only other defect likely to occur is bad formation due to insufficient venting of the die, or to lack of adequate thermal balance in the cavity. Experienced observation of the job as a whole will indicate what is likely to prove the best remedy, and suitable venting and/or overflow wells should then be added accordingly.

It must be emphasized that, during the try-out, apart from the initial run for the purpose of obtaining samples for dimensional check only, the most important requirement is to ensure a steady high operating rate once the die is up to working temperature, and a sufficiently long

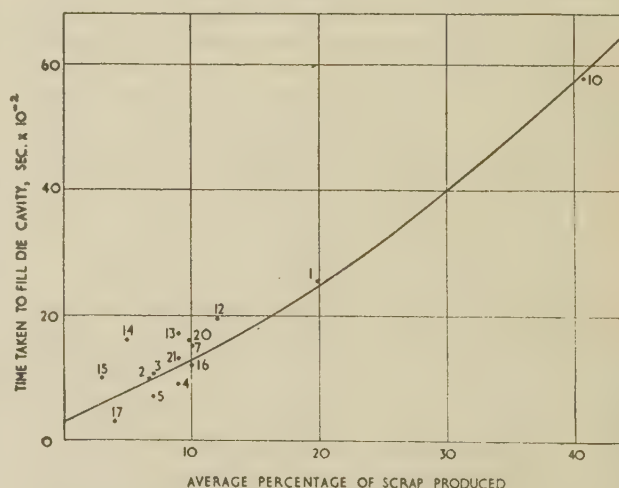


FIG. 6.—Relationship Between Time Taken to Fill Die Cavity and Percentage of Scrap Produced.

run between any one change and the next to ensure that all the conditions have become stabilized at their natural levels. If this is not done, completely erroneous results will be obtained, and often unnecessary alterations made to the die or to the procedure as a whole.

When it has been decided that the optimum operating



conditions have been determined, these should be recorded and used on all future occasions.

As a test, a series of twenty-one typical aluminium pressure die-castings was surveyed from the point of view of average percentage of scrap produced when the operating conditions were held at optimum values for the dies concerned. The relationships between the variables injection speed, pressure, cavity-filling times, and quality—as represented by minimum scrap figures achieved—were plotted. No connection appeared to exist between injection pressure and any other variable, and it was therefore concluded that this factor was of no direct significance. It has subsequently been found that the manner in which the pressure varies throughout the

jection speed and pressure, as well as the metal temperature, will also have been set to predetermined values. The only variables left to the operator are thus the time taken in ladling from the holding pot and injecting the metal into the die, the time interval between each casting cycle when the operator is cleaning and dressing the die, and the setting of the valves controlling the water-cooling.

The water cooling is best controlled by arranging that all water lines from each half of the die are connected to two common manifolds, ingoing and outgoing. Valves on the individual lines may then be set once and for all, and the whole of the water cooling turned on or off by main valves on the manifolds. Connection is also made direct to the manifold when setting up the die in the machine. Only two connections are thus necessary on each die half, instead of two to each water line.

The time interval between each casting cycle and the general rhythm of operation will be largely controlled by the fact that a time study has been made of the job and that the operator will be working to a recommended rate.

The time taken in ladling the metal from the holding pot into the sleeve and then injecting the metal into the die, will be varied by the operator to allow for slight differences in metal temperature, metal composition, and die temperature, and will serve as the "fine adjustment" on the casting cycle. The main points to be borne in mind are that a ladle of the same size should always be used on a given job and that the size should be such that when the ladle is filled to within about  $\frac{1}{2}$  in. of its brim the casting is made with a slug about  $\frac{3}{4}$  in. long. It is important that a uniform amount of metal is ladled each time. The metal in the pot must be kept clean and the surface free from excessive dross build-up; it should be agitated as little as possible and the surface skin gently parted with the back of the ladle each time metal is ladled from the pot. This ladleful of metal should then be carefully poured in a continuous stream, again with as little agitation as possible, into the injection sleeve. The practice of violently stirring the pot of metal with the ladle in order to clean off the ladle skulls cannot be too strongly deprecated, as it leads to excessive dross inclusion and consequently sluggish metal.

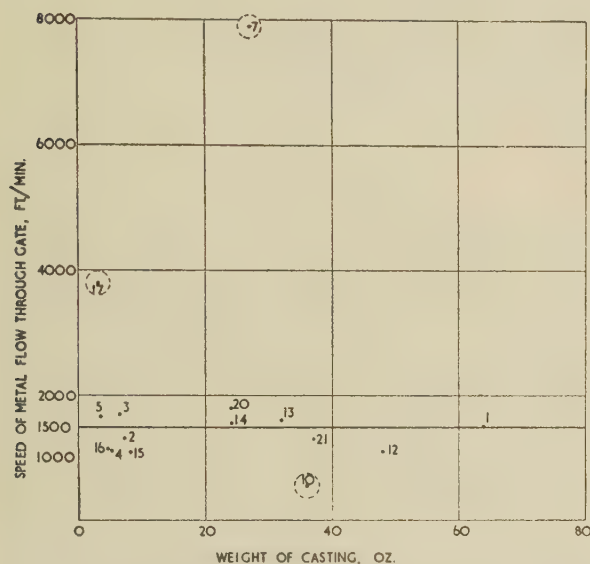


FIG. 7.—Relationship Between Speed of Flow of Metal Through the Gate and Surface Finish of Castings of Various Weights. The horizontal line at 1500 ft./min. represents the optimum speed of metal flow. Castings 7, 10, and 17 showed persistent surface blemishes.

stroke is of more importance. The most significant correlation was found between the time required to fill the cavity and the percentage of scrap produced (see Fig. 6). The rate of flow through the gate also was found to be related to the quality of surface of the castings (see Fig. 7).

## X.—PRODUCTION RUNNING OF THE DIE

Once the casting operation has begun, it should be allowed to proceed at a steady rate for as long as possible, under uniform and standard conditions. The second most important factor is to ensure that the minimum amount of lubricant only is used on the die faces, ejectors, and injection sleeve and plunger. Assuming that a suitable die design and casting design have been evolved, the two most common causes of scrap are erratic die operation and excessive lubrication.

All phases of the machine cycle should have been previously set, by means of auto-timers, to values found to be optimum during the die try-out period. The in-

## XI.—INSPECTION PROCEDURE

One of the most important aspects of operator technique is the maintenance of a steady rhythmic cycle of movements. Nothing is more likely to interrupt this cycle than for the operator to have critically to examine his work as he is producing it. A cursory visual inspection of each casting as it is taken from the machine may be desirable, but detailed control of quality must be left to the Inspection Department.

It is, moreover, of fundamental importance that inspection should be integrated with the production procedure in such a way as to maintain casting conditions within the limits required to ensure that unsatisfactory castings are not produced. This is the positive approach, as opposed to the negative one of merely making certain that no defective castings leave the foundry. It means that the inspector must carry out a regularly timed visual and dimensional check as the castings are being

made, and that wherever such checks show that quality is deteriorating, die temperature, metal temperature, injection pressure and speed, &c., must be compared with the record card. In this way immediate remedial action can be taken to bring the job back within control limits. A 100% inspection is usual with large castings, but with smaller castings this may be reduced to as low as 10%, provided that the check is made at fixed intervals.

In certain cases, it may even be necessary for full-time

inspection to be maintained on a particular die-casting machine. For example, in the production of die-cast sole plates for electric irons, it is desirable to inspect and fully test electrically every casting as it is produced, and a similar procedure may be applied to die-cast squirrel-cage rotors for induction motors. Before these electrical tests can be carried out, fettling and machining operations have first to be completed, and such operations are therefore also made part of the inspection procedure.



# THE MECHANISM OF FATIGUE FAILURE IN SOME BINARY AND TERNARY ALUMINIUM ALLOYS\*

1753

By P. J. E. FORSYTH,† A.I.M., MEMBER, and C. A. STUBBINGTON,† A.I.M., MEMBER

## SYNOPSIS

The fatigue process in a number of aluminium alloys was found to be one of depletion of solute atoms in localized regions under the action of cyclic stresses. The depletion or overageing produced soft spots in the structure, in which most of the subsequent plastic deformation was concentrated. It appeared that the temperature range was important in determining whether the depleted zones were trans- or inter-crystalline and the subsequent fatigue cracks followed these paths. A crack once started might, by virtue of the heavy stress concentration, produce its own depleted zone ahead of the root, and could thus progress without reference to existing soft spots.

## I.—INTRODUCTION

EARLIER work<sup>1</sup> has shown that a number of binary aluminium alloys which may be described as ageing systems exhibit a phenomenon called slip-band extrusion. This phenomenon is associated with a particularly "brittle" type of fracture, and it was concluded that this was the result of the formation of zones depleted of solute atoms. It was emphasized that slip-band extrusion is not a necessary part of the fatigue process but rather is it a visible by-product of the depletion effect and in certain circumstances is not observed, although brittle fracture may still occur. This slip-band extrusion suggested the soft nature of these zones, which is consistent with the formation of a solid solution of equilibrium concentration. In order to obtain further information regarding the nature of the zones, a study has been made under various conditions on alloys chosen to represent a wide range of ageing rates.

## II.—EXPERIMENTAL PROCEDURE

### 1. MATERIALS

The materials used were:

- (i) Aluminium-4% copper, extruded and rolled.
- (ii) Aluminium-10% zinc, forged and rolled.
- (iii) Aluminium-8% silver, extruded and rolled.
- (iv) Aluminium-4% copper-0.05% tin.
- (v) Aluminium 3.1% copper-1.3% magnesium.

The last two alloys were kindly supplied by Dr. H. K. Hardy, late of the Fulmer Research Institute.

All the material was finally cold rolled to 0.025 in., the specimen thickness. Specimens, 0.075 in. long  $\times$  0.325 in. wide, and containing a stress-raiser to localize the deformation, were cut from the strip and solution-treated and quenched into water at room temperature, unless otherwise stated. The specimens were electro-

polished immediately before testing, the polishing process removing approximately 0.005 in. from the central area of the specimen.

The solution-treatment time was in most cases 1 hr. A preliminary survey of the effect of solution-treatment time was made and no difference in the microscopical effects of fatigue stressing could be detected between specimens solution-treated for 1 hr. or for 16 hr., although, as will be described later, there is reason to believe that in certain cases the degree of homogeneity may influence the mode of failure.

### 2. APPARATUS

A small vibrator was constructed to fatigue the specimens at room temperature and temperatures up to 300° C. It consisted of an electromagnet bolted to a rigid vertical plate. Power was supplied to the coil of the electromagnet by a power amplifier driven by a decade oscillator. The specimen had a soft-iron armature fixed to its free end and was vibrated by the electromagnet at resonance.

The fixed end of the specimen was held by a retaining screw in a furnace block. This screw also served to fix a thermocouple on the outside of the block. The thermocouple was calibrated under static conditions against a thermocouple fixed to the specimen in the region of the stress-raiser and found to agree within  $\pm 5^\circ$  C. The furnace block was heated by means of a flat Nichrome element clamped between mica sheets. A sheet of asbestos heat-resisting material insulated the element from the supporting bracket.

The stress on the specimen was estimated from the amplitude of vibration of the specimen. This value was used only as a guide to ensure that specimens would fail within a reasonable time. As this investigation was of a metallographic nature, and the specimens were small, it was considered that a greater accuracy of stress measurement would serve no useful purpose. The estimated value of the fatigue stress used for most of the tests was

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$\pm 12$  tons/in.<sup>2</sup>; this produced lives of the order of  $10^5$  cycles.

### III.—EXPERIMENTAL RESULTS

#### 1. ROOM-TEMPERATURE FATIGUE TESTS

Room-temperature tests on solution-treated aluminium-4% copper and aluminium-10% zinc alloys have already been reported.<sup>1</sup> In all cases slip-band extrusion was produced and, in addition, the aluminium-10% zinc alloy showed some grain-boundary cracking.

The effect of room-temperature fatigue stresses on solution-treated and quenched aluminium-4% copper-0.05% tin alloy is shown in Fig. 1 (Plate LIII). Slip-band extrusion occurred in the material to a degree comparable with that found on the aluminium-4% copper alloy fatigued under the same conditions. A similar type of extrusion was observed in aluminium-3.1% copper-1.3% magnesium alloy.

It was observed that the main crack did not always show ribbon along its edges. It is possible that extrusion had occurred along the main crack, but that the ribbon was disintegrated by hammering and attrition. This attrition also produced a loose, flocculent deposit along the edges of the main crack, the volume of which was dependent on the crack configuration, i.e. whether rubbing of the fracture surfaces could occur.

#### 2. LOW-TEMPERATURE FATIGUE TESTS

It had been found earlier<sup>1</sup> that in aluminium-4% copper alloy the slip-band extrusion effect could be suppressed by fatiguing at reduced temperatures. This suggested that the rate at which the alloy aged was the criterion of the extrusion effect. To investigate this, the two ternary alloys, which age more rapidly than aluminium-4% copper alloy, were tested at low temperatures. It was found that the extrusion effect could not be suppressed in the aluminium-3.1% copper-1.3% magnesium alloy, even at liquid-nitrogen temperature. This was consistent with the observations made on the aluminium-10% zinc alloy, which also ages rapidly. Fig. 2 (Plate LIII) shows extrusion near the main fracture in the aluminium-copper-magnesium alloy fatigued in the solution-treated condition at  $-195^\circ\text{C}$ . The aluminium-4% copper-0.05% tin alloy, when fatigued at liquid-nitrogen temperature, showed no extrusion, and the marked striations typical of the aluminium-4% copper alloy fatigued even at  $-25^\circ\text{C}$ . were not observed. Instead, it was found that deformation marks which occasionally appeared as very narrow striations were the only surface features. Fig. 3 (Plate LIII) shows the deformation observed when aluminium-4% copper-0.05% tin was fatigued at  $-195^\circ\text{C}$ . Arrow *A* (Fig. 3) indicates that the markings apparently outline a substructure. This effect was observed in pure aluminium fatigued at low temperature and has already been reported.<sup>2</sup> It is considered that this alloy behaves in a manner intermediate between the aluminium-4% copper and aluminium-10% zinc alloys, while the other ternary alloy, aluminium-copper-magnesium, behaves similarly to the aluminium-10% zinc alloy.

It had been previously noticed that in the case of

aluminium-4% copper alloy an intermediate state existed in the mode of fracture at about  $0^\circ\text{C}$ . Visible extrusion was suppressed at this temperature, but no striations were observed, the material cracking in the brittle manner of the room-temperature failure.

As the ageing was obviously an important factor, it was considered that the period at room temperature after quenching and before the start of the low-temperature test was probably affecting the subsequent deformation. It has already been shown<sup>1</sup> that a short ageing treatment induced the extrusion effect in aluminium-8% silver alloy. It was therefore decided to test the rapid-ageing materials directly after quenching into liquid nitrogen, with no subsequent period at room temperature. Aluminium-3.1% copper-1.3% magnesium alloy was therefore quenched from  $505^\circ\text{C}$ . into liquid nitrogen and fatigued at that temperature, and it was found that the extrusion effect could be suppressed by this treatment. Quenching specimens of aluminium-10% zinc alloy into liquid nitrogen and immediately fatiguing at that temperature, however, did not suppress the slip-band extrusion effect.

#### 3. ELEVATED-TEMPERATURE FATIGUE TESTS

Aluminium-10% zinc alloy, when fatigued at room temperature, not only exuded material from the slip bands and cracked across the grains, but it also showed a certain amount of intercrystalline cracking. It was considered that if a similar depletion of solute atoms occurred at the grain boundaries as that which was believed to produce the slip-band extrusion, then brittle boundary conditions would exist. This depleted grain-boundary condition has been investigated by Perryman and Blade<sup>3</sup> and has been suggested as the cause of delayed boundary cracking and also of corrosion in certain light alloys. To investigate this effect, a series of elevated-temperature fatigue tests have been carried out on a number of simple alloys. It was found that boundary fatigue cracking occurred in a number of these alloys within certain ranges of temperature. Generally speaking, low temperatures tend to suppress slip-band extrusion and the higher temperatures induce boundary cracking. The width of the affected grain boundary increases with temperature, and under these conditions a form of block extrusion occurs. This form of extrusion also occurs along the active slip bands.

With the exception of the aluminium-copper-magnesium alloy, which seemed to show no brittle boundary condition, the increased ageing rate reduced the temperature at which grain-boundary failure was active. The fact that the exception is the aluminium-copper-magnesium alloy suggests that the criterion is not the precipitation but the depletion which accompanies it. In the case of this alloy, even after depletion of the copper, the matrix may be relatively hard owing to the other more stable solute atoms present. These remaining solute atoms will also tend to inhibit recrystallization of the depleted zone. The different types of deformation and fracture are shown in Figs. 4-7 (Plate LIII). Fig. 4 illustrates the thick slip-band eruption that occurs in aluminium-4% copper alloy fatigued at  $250^\circ\text{C}$ . When such a region was repolished electrolytically, it could be seen that a depleted zone had been produced, and it was this zone that had been partially



extruded. Fig. 5 shows a depleted slip zone. The grain boundaries of such specimens also showed these eruptions in zones of copper depletion and were in this respect similar to the slip-band regions. Fig. 6 shows a typical boundary eruption, and Fig. 7 the microstructure after repolishing. The formation of these depleted zones will be discussed later. Some grain-boundary failure also occurred in aluminium-4% copper-0.05% tin after fatiguing at 300° C., with clearly defined depleted zones and precipitation along the grain boundaries.

The aluminium-10% zinc alloy, which produced some intercrystalline cracking at room temperature, showed a certain amount of eruption along the slip bands when fatigued at 100° C. (Fig. 8, Plate LIII), together with a tendency to form striations similar to those observed in aluminium-2% zinc alloy fatigued at room temperature. When this material was fatigued at 150° C., it behaved in a very similar manner to pure aluminium, although at this temperature a large degree of boundary deformation and migration occurred. This is shown in Fig. 9 (Plate LIV). The boundary deformation at these temperatures is no doubt due to the polygonization and creep that occurs in these regions.

#### 4. DEPLETED ZONES PRODUCED BY FATIGUE COMPARED WITH THE MORE COMMON DISCONTINUOUS TYPE OF PRECIPITATION

It is well known<sup>4,5</sup> that quenching an alloy after solution-treatment produces strain in the form of slip in the material, and subsequently precipitation is very rapid in these regions. During a hot fatigue test this rapid discontinuous precipitation may occur, outlining the slip bands produced by quenching (*A*, Fig. 10, Plate LIV). Where the fatigue stresses are higher, the original slip regions are destroyed and the precipitation is of a more homogeneous form, with no visible crystallographic preferences (*B*, Fig. 10). In regions where the fatigue stresses are large enough, new sets of bands become visible, which are the depleted zones previously described (*C*, Fig. 10). It can be seen that the grain boundaries in this more highly stressed region of the specimen are also depleted.

#### 5. EFFECT OF PRIOR HOT FATIGUE ON SUBSEQUENT DEFORMATION IN ALUMINIUM-4% COPPER ALLOY

It was found that the depleted zones produced by fatigue at elevated temperatures showed heavy localized deformation when subsequently fatigued at room temperature. In some regions a thick extrusion took place from the depleted slip-band zones, as shown in Fig. 11 (Plate LIV). Heavy localized deformation also occurred at grain boundaries. The same effects were present with subsequent static stress with the exception of the extrusion; again the deformation was localized in the depleted zones and was in the form of narrower and straighter strain marks. In Fig. 12 (Plate LIV) it can be seen that the static deformation is very sharply defined along the depleted slip-band zone. It would also appear that the shearing occurs mainly at the interface between the soft zone and the harder matrix, rather than in the middle of the soft area.

#### 6. EFFECT OF LIQUATION OF CONSTITUENTS DURING SOLUTION-TREATMENT ON SUBSEQUENT FATIGUE BEHAVIOUR

It is generally assumed that liquated constituents at grain boundaries are detrimental to the fatigue properties of the alloy. To investigate the effect of boundaries containing a hard brittle constituent, specimens of aluminium-4% copper alloy were overheated by solution-treating at 575° C. to produce typical liquation with an almost continuous network of  $\text{CuAl}_2$  at the grain boundaries. The subsequent fatigue stresses produced transcrystalline failure with some slip-band extrusion. No grain-boundary deformation and cracking was seen, and, in fact, even when cracks crossed grain boundaries no subsidiary cracks were observed following the boundary film of  $\text{CuAl}_2$ . Fig. 13 (Plate LIV) shows cracks crossing a grain boundary where a  $\text{CuAl}_2$  film exists. These observations on the relatively harmless nature of the liquated boundary phase under fatigue conditions have also been made in commercial alloys, including D.T.D.683 (aluminium-zinc-magnesium alloy).

#### 7. EVIDENCE FOR DEPLETED ZONES PRODUCED BY CYCLIC STRESSES

The observations described above on the effects of fatigue on various alloys at various temperatures suggests that cyclic stressing induces an ageing process. For the detection of depleted zones, etching reagents are open to question, as it could be argued that these zones will be subjected to a high degree of deformation and would, by virtue of this alone, be liable to etch differently. The relatively wide depleted zones produced by fatiguing at elevated temperatures present no problem and can easily be observed microscopically without resort to etching. As the width of these zones increases with increasing temperature, it is reasonable to assume that the changes which have been detected along all slip zones where extrusion has occurred are of a similar nature. It is well known that if statically deformed material is subsequently aged, discontinuous precipitate occurs along slip bands. The subsequent ageing of room-temperature fatigued material, on the other hand, showed depletion along slip regions, as has been illustrated earlier.<sup>1</sup> Fig. 14 (Plate LIV) shows an aluminium-4% copper specimen which has been fatigued at room temperature and, without subsequent repolishing, aged in air at 240° C. for 3 hr. The difference in surface staining is considered to be an indication of the copper content. It can be seen that the active slip bands which produced the slip-band extrusion coincide with the depleted zones.

#### 8. CRACK PROPAGATION

It has already been shown<sup>1</sup> that transcrystalline cracking can occur at an angle to the operative slip planes and, by using the same technique as that outlined above, depleted zones could be detected along which the cracks were progressing. It was also found that the heavy stress concentration produced by boundary sliding and cracking could produce a depleted zone in a neighbouring crystal through which the crack was propagated. This is illustrated in Fig. 15 (Plate LIV), from which

it can be seen that the depleted zone and associated crack may not necessarily follow a crystallographic direction, but may be entirely dependent on the stress concentration present in the microstructure.

#### IV.—DISCUSSION

##### 1. THE SOLUTE-ATOM DEPLETION PROCESS UNDER THE ACTION OF CYCLIC STRESSES

The formation of depleted zones in regions of stress concentration and the subsequent heavy localized deformation in these regions would seem to constitute the mechanism of fatigue failure in age-hardening alloys. The possible reason for the formation of a depleted zone will now be discussed. It has already been suggested that cyclic stresses may induce polygonization or recovery by increasing the self-diffusion rate in certain crystal regions by the production of vacant lattice sites.<sup>1, 6, 7</sup> By this same process, local ageing will occur owing to the diffusion of solute atoms. This ageing will eventually produce small depleted zones in the more highly stressed regions of the crystal.

The fact that diffusion takes place so rapidly under the action of cyclic stresses can be partly explained by the high strain rates that may occur. It has been shown that the rate of self-diffusion in  $\alpha$ -iron depended primarily on the strain rate, rather than on the amount of strain applied.<sup>7</sup> This was explained by the fact that edge dislocations may serve as both sources and sinks for lattice vacancies, which may be generated in large numbers by an avalanche movement of dislocations. As there is considered to be an equilibrium number of vacancies for any given temperature, the number that can exist in the lattice will depend on the rate at which they are generated. Thus, high strain rates may generate an excess number, the concentration of which will control the diffusion rates in heavily deformed zones. It is considered that the initial depleted zones will be along the operative slip planes and that they will be influenced by any pre-existing inhomogeneities in the solid solution.

##### 2. PRE-EXISTING INHOMOGENEITIES IN THE SOLID SOLUTION

It has been observed<sup>1</sup> in aluminium-silver alloys that the application of cyclic stress after solution-treatment at a temperature well within the  $\alpha$  solid-solution range produces fatigue deformation very similar to that produced in pure aluminium fatigued in the annealed condition. Material solution-treated at a temperature just above the solubility line, however, produces slip-band extrusion when fatigued at room temperature. The slip-band extrusion effect can also be produced on specimens solution-treated well within the  $\alpha$  solid-solution range, if a short ageing treatment is given before fatiguing.

The observations suggest that if a high degree of disorder is produced in the lattice by prior heat-treatment, then the subsequent fatigue deformation of the material is similar to that of a pure metal. If, on the other hand, a degree of order—produced either by earlier heat-treatment or subsequent fatigue—exists in the lattice, then with further application of cyclic stress disordering may

occur on certain active slip bands, leading to the production of soft spots and a subsequent larger-scale depletion process with accompanying extrusion.

It has been shown by Walker and Guinier and by others<sup>8, 9</sup> that ordering of the solute atoms can be detected by X-ray methods in the aluminium-silver and aluminium-zinc systems. Rudman *et al.*<sup>9</sup> have examined by X-ray methods an alloy of aluminium-20 at.-% zinc, held at 400° C., and found that ordering or clustering of the zinc atoms occurs at this temperature. Whereas each zinc atom should have 2/4 nearest neighbours on a random basis, the measured number is 3/7. They conclude that this is evidence for ordering or clustering of the zinc atoms at a temperature above which precipitation of the zinc should occur. It is considered that the present work confirms this ordering effect in the solid solution, in view of the differences in fatigue behaviour in some of the alloys investigated when heat-treated at different temperatures within the solution range.

##### 3. OCCURRENCE OF SHARPLY DEFINED TRANSCRYSTALLINE CRACKING WITH NO ACCOMPANYING SLIP-BAND EXTRUSION

There would seem to be a lower limit to the thickness of material extruded, i.e. a lower limit to the width of the depleted zone. Below this width or thickness, the zone ruptures with no evidence of extrusion. This is consistent with the fact that the wider the depleted zone, the more creep can occur, and the narrower the zone, the greater the stress concentration and the greater the chance of brittle fracture.

##### 4. EFFECT OF LIQUATION DURING SOLUTION-TREATMENT ON SUBSEQUENT FATIGUE BEHAVIOUR

The existence of a brittle boundary film of  $\text{CuAl}_2$  did not induce grain-boundary cracking. In fact, fatigue cracks were invariably transcrystalline and even when a crack crossed a grain boundary where a  $\text{CuAl}_2$  film existed, there was no evidence of the crack path being deflected along the boundary. This suggests that, at least where cohesion is good, a brittle phase of the nature of  $\text{CuAl}_2$  is not detrimental, even when existing as a thin boundary film. This observation has also been confirmed on D.T.D. 683 alloy, in which the liquated phase can be resolved as a fine eutectic. Further work has shown that, as would be expected, impact values are greatly reduced by the presence of complete boundary liquation.

#### V.—CONCLUSION

The present study of the fatigue behaviour of a number of simple aluminium alloys at various temperatures, together with earlier observations,<sup>1, 2</sup> suggests that the fatigue of aluminium and its alloys is closely associated with the formation of soft spots in the metal crystals. These microscopical changes are caused by the action of the cyclic stresses. In the case of pure aluminium, the striations represent the regions where deformation continues to occur during the test. In cold-rolled pure aluminium this softening manifests itself more clearly as



small recrystallized zones, and in the alloys examined in the present work the soft spots are produced in the form of depleted zones, presumably of the composition in equilibrium at the fatigue temperature. When the soft spots are formed, the deformation becomes extremely localized and the final rupture involves the aggregation of a high density of vacant lattice sites. The diffusion of the copper atoms from the deformed regions can be considered as a shaking-down process by which the aluminium lattice becomes less strained. This tendency to lower the strain energy in the regions of glide allows further plastic deformation to be accommodated.

The formation of a hard brittle phase at the grain boundaries, either as eutectic or a continuous film, did not embrittle the boundaries; the fracture still occurred by the formation of transcrystalline depleted zones and accompanying slip-band extrusion.

## ACKNOWLEDGEMENT

Acknowledgement is made to the Controller, H.M. Stationery Office, for permission to publish this paper.

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## NOTICE TO AUTHORS OF PAPERS FOR THE "JOURNAL" AND CONTRIBUTORS TO DISCUSSIONS

1. **Papers will be considered for publication from non-members as well as members of the Institute.** They are accepted for publication in the *Journal* and not necessarily for presentation at any meeting of the Institute. MSS. should be addressed to The Editor of the *Journal*, The Institute of Metals, 17 Belgrave Square, London, S.W.1.

2. **Papers suitable for publication** may be classified as:

(a) Papers recording the results of original research.

(b) First-class reviews of, or accounts of progress in, a particular field.

(c) Papers descriptive of works, methods, or recent developments in metallurgical plant and practice.

(d) Papers in classes (a), (b), and (c) above, previously published in languages other than English, French, German, or Italian, if of sufficient merit.

3. **Manuscripts and illustrations** should be submitted in duplicate. MSS. must be typewritten (*double-line spacing*) on one side of the paper only, and authors are requested to sign a declaration that neither the paper nor a substantial part thereof has been published elsewhere. Exceptions may be made in certain cases where a paper has been published in a language other than English, French, German, or Italian (see 2(d) above). MSS. not accepted are normally returned within 6 months of receipt.

In the interests of economy, all papers must be written as concisely as possible; in general, internal research reports are not in suitable form for publication as papers in the *Journal*. All but the simplest mathematical expressions should be written by hand, with capital and small letters clearly distinguished. Superscript and subscript letters should also be plainly indicated. Greek letters and special signs should be identified in the margin. For style, spelling, and abbreviations used, any recent issue of the *Journal* may be consulted.

4. **Synopsis.** Every paper must have a synopsis (not exceeding 250 words in length) which, in the case of a paper reporting original research, should state its objects, the ground covered, and the nature of the results. The synopsis will appear at the beginning of the paper, and should be in a form suitable for use by abstracting organizations. Extracts from a "Guide for the Preparation of Synopses" drawn up by the Abstracting Services Consultative Committee are reproduced below.

5. **References** must be collected at the end of the paper and must be numbered in the order in which they occur in the MS. Initials of authors must be given, and the Institute's official abbreviations for periodical titles (as used in *Metallurgical Abstracts*) should be employed, where known. References to papers should be set out in the style:

A. L. Dighton and H. A. Miley, *Trans. Electrochem. Soc.*, 1942, **81**, 321 (i.e. year, volume, page).

References to books should be in the following style:

C. Zener, "Elasticity and Anelasticity of Metals". 1948: Chicago (University of Chicago Press).

6. **Illustrations.** Each illustration must have a number and description; only one set of numbers must be used in one paper, and it is desirable to number the half-tone illustrations consecutively, rather than to intersperse them with the line figures. The captions should be typed on a separate sheet.

The set of **line figures** sent for reproduction must be drawn (about twice the size to appear in the *Journal*) in Indian ink on smooth white Bristol board, good-quality drawing paper, co-ordinate paper, or tracing cloth, which are preferred in the order given. Co-ordinate paper, if used, must be blue-lined with the co-ordinates to be reproduced finely drawn in Indian ink. Curves should be drawn boldly (i.e. at least twice the thickness of the frame). Experimental points should be indicated by open or closed circles, triangles, squares, &c. (preferably not crosses). Curves should be broken on each side of such symbols and plenty of allowance should be made for closing up in blockmaking. All lettering and numerals, &c., should preferably be in pencil, so that the Institute's standard lettering may be affixed, and ample margins must be left outside the framework of the figures to enable this to be done. The second set of line illustrations may be photostat copies.

**Photographs** must be restricted in number, owing to the expense of reproduction, and photomicrographs should be trimmed to the smallest possible of the following sizes consistent with adequate representation of the subject: 4 in. deep by 3 in. wide: 2 in. deep by 3 in. wide: 2 in. square. Magnifications of photomicrographs must be given in each case. Photographs for reproduction should be loose, not pasted down (and not fastened together with a clip, which damages them), and the figure number and author's name should be written on the back of each. Captions should be given to the photomicrographs, but these should be kept as brief as possible.

Because of the present high cost of printing and paper it is imperative that authors restrict illustrations (particularly photographs) to the absolute minimum deemed necessary to support their argument. Only in exceptional cases will illustrations be reproduced if already printed and readily available elsewhere.

7. **Tables or Diagrams.** Results of experiments, &c., may be given in the form of tables or figures, but (unless there are exceptional reasons) not both. Tables should bear Roman numbers, and each should have a heading that will make the data intelligible without reference to the text.

8. **Corrections.** A certain number of corrections in proof are inevitable, but any modification of the original text is to be avoided. Since corrections are very expensive, the Institute reserves the right to require authors to contribute towards their cost if the Editor deems them to be excessive. The Institute also reserves the right to require a contribution to the cost of remaking any block where this is necessitated by an error on the author's part.

9. **Reprints.** Individual authors are presented with a maximum of 25, and two or more authors with a maximum of 50 reprints from the *Journal*, without covers. Limited numbers of additional reprints can be supplied at the author's expense, if ordered before proofs are passed for press. (Orders should preferably be placed when submitting MSS.)

10. **Discussion.** Except in the case of special symposia, shorthand records of discussions are not taken at meetings. Written discussion may be submitted on any paper, preferably typewritten (*double-line spacing*). References should be given in the form of footnotes. Paragraphs 6 and 7 above are also applicable to such contributions. Reprints of discussion cannot be supplied to contributors.

### GUIDE FOR THE PREPARATION OF SYNOPSES

(As recommended by the Abstracting Services Consultative Committee)

1. **Purpose.** The synopsis is not part of the paper; it is intended to convey briefly the content of the paper, to draw attention to all new information, and to the main conclusions. It should be factual.

2. **Style of writing.** The synopsis should be written concisely and in normal rather than abbreviated English. It is preferable to use the third person. Where possible use standard rather than proprietary terms, and avoid unnecessary contracting.

It should be presumed that the reader has some knowledge of the subject, but has not read the paper. The synopsis should therefore be intelligible in itself without reference to the paper; for example, it should not cite sections or illustrations by their numerical references in the text.

3. **Content.** The title of the paper is usually read as part of the synopsis. The opening sentence should be framed accordingly and repetition of the title avoided. If the title is insufficiently comprehensive, the opening should indicate the subjects covered. Usually the beginning of a synopsis should state the objective of the investigation.

It is sometimes valuable to indicate the treatment of the subject by such words as: brief, exhaustive, theoretical, &c.

The synopsis should indicate newly observed facts, conclusions of an

experiment or argument and, if possible, the essential parts of any new theory, treatment, apparatus, technique, &c.

It should contain the names of any new compound, mineral species, &c., and any new numerical data, such as physical constants; if this is not possible, it should draw attention to them. It is important to refer to new items and observations, even though some are incidental to the main purpose of the paper; such information may otherwise be hidden, though it is often very useful.

When giving experimental results the synopsis should indicate the methods used; for new methods the basic principle, range of operation, and degree of accuracy should be given.

4. **References.** If it is necessary to refer to earlier work in the summary, the reference should always be given in full and not by number. Otherwise references should be left out.

When a synopsis is completed, the author is urged to revise it carefully, removing redundant words, clarifying obscurities, and rectifying errors in copying from the paper. Particular attention should be paid by him to scientific and proper names, numerical data, and chemical and mathematical formulae.



# REPORT OF COUNCIL

## FOR THE YEAR ENDED 31 DECEMBER 1956

THE year 1956 proved to be a most important one in the Institute's history, and the Council is pleased to be able to report a further substantial increase in the Institute's membership.

As members will be aware, from notices published in the *Bulletin*, through the generosity of many companies in the metallurgical and engineering industries and with the help of individual contributions of many members, the Institute has been able to acquire an eighty-year lease of No. 17 Belgrave Square, London, S.W.1, and furnished it as a new Headquarters at an approximate cost of £55,000. The rapid growth in the Institute's membership and activities since the war had made it impracticable for the offices to remain at No. 4 Grosvenor Gardens, where the maximum amount of available accommodation was in use, and, in fact, the administration was in danger of a breakdown because of the cramped conditions of work and storage.

The Institute's new Headquarters, of which a photograph is included in this report, is one of which all members may be justly proud. It provides adequate space for future growth and development. In addition to the administrative offices, the new Headquarters contains beautifully designed and handsomely furnished Council and Committee rooms, a well-equipped meeting room for scientific meetings, and a most comfortable members' reading and writing room.

The Council desires to place on record its gratitude to all those who have so generously contributed to the cost of acquiring the lease and the furnishing of the new Headquarters. No general appeal is being made for subscriptions in aid of this new venture. Contributions towards the cost, amounting to approximately £40,000, have been received and further donations from members and other interested Companies are anticipated.

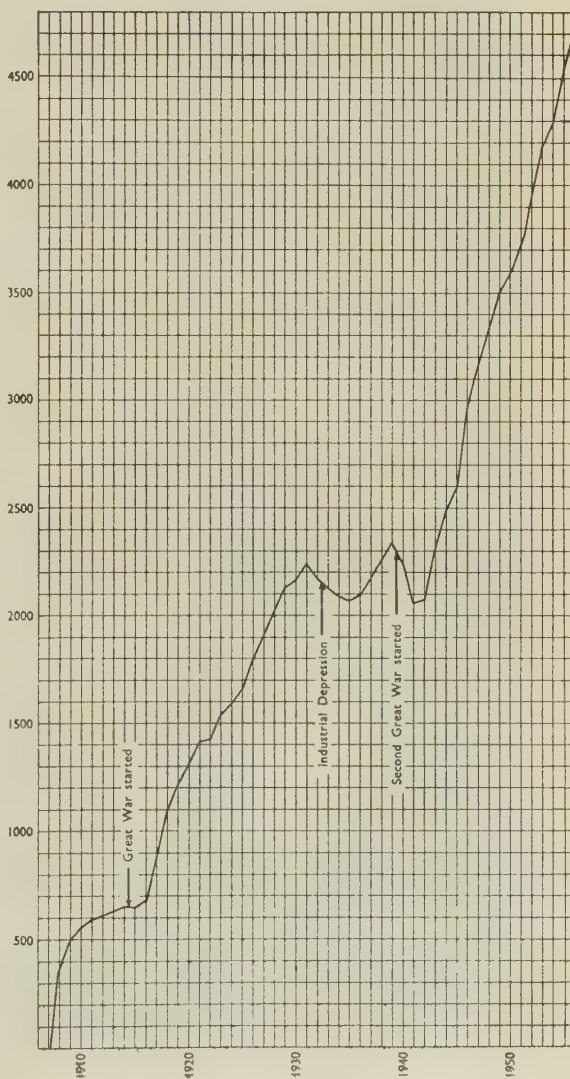
The Council has expressed to the Iron and Steel Institute, and its Secretary and staff, its gratitude for many courtesies received and the close collaboration which has existed during the many years in which both societies have been jointly in occupation of No. 4 Grosvenor Gardens.

By agreement with the Iron and Steel Institute, the Joint Library will remain at Grosvenor Gardens.

The Autumn Meeting was held in Germany, at Stuttgart and Frankfurt-am-Main, by invitation of the Deutsche Gesellschaft für Metallkunde. For part of the time, it was a joint meeting between the two societies, and was an unqualified success. The Council records its gratitude to the German society

for its invitation, and to all those who did so much to ensure the excellence of the arrangements made. In particular, it expresses its warm thanks to Professor Dr. P. Brenner, Professor Dr. W. Köster, and Dr. Max Hansen, each of whom made major contributions to the success of the meeting.

The Council is pleased to announce that the Institute has received, and accepted, an invitation to become a member of the British Nuclear Energy Conference, further particulars of the objects and activities of which will be published in the *Bulletin* in due course.



Active Membership at 31 December 1908-1956.



THE INSTITUTE'S NEW HEADQUARTERS  
17 Belgrave Square, London, S.W.1.



## MEMBERSHIP

There was a net increase in membership of 182 during the year. In the period under review, the Overseas Sustaining Membership Scheme came into force, and the Council is glad to report that already 38 companies, with headquarters located outside the United Kingdom, have decided to give financial support to the work of the Institute by taking out this class of membership.

The growth in membership in the past eight years is shown in the following table :

At 31 December	1949	1950	1951	1952	1953	1954	1955	1956
Honorary Members . .	11	11	11	11	11	11	11	11
Fellows . .	9	10	8	8	9	9	10	11
Overseas Sustaining Members .	...	...	...	...	...	...	...	38
Ordinary Members .	2685	2815	2941	3144	3368	3508	3780	3808
Junior Members .	...	291	305	362	363	293	258	292
Associate Members .	18	...	...	...	...	...	...	...
Student Members .	783	452	462	423	417	457	470	551
Active List .	3506	3579	3727	3948	4168	4278	4529	4711
Suspense List .	67	97	124	95	131	157	118	152
TOTAL . .	3573	3676	3851	4043	4299	4435	4647	4863

## ORIGINAL MEMBERS : ELECTION TO HONORARY LIFE MEMBERSHIP

In recognition of their long support of the Institute's objects and work, the Council elected to Honorary Life Membership the following Original Members whose names were on the roll on 21 March 1956 :

ANDREW, Professor Emeritus J. H., D.Sc.  
 BAMFORD, Mr. C. C.  
 CLAMER, Dr. G. H., B.S. (U.S.A.).  
 COOKSON, Mr. Clive.  
 DESCH, Dr. C. H., F.R.S. (*Past-President and Fellow*).  
 DRURY, Mr. H. J. H. (Australia).  
 FÉRON, Mr. Albert (Belgium).  
 GARNHAM, Mr. F. M.  
 GREENWOOD, Mr. H. W.  
 GWYER, Dr. A. G. C., B.Sc.  
 HIGHTON, Mr. D. C., M.A.  
 HOLT, Mr. H.  
 HUMPHREYS, Mr. T. C.  
 HUTTON, Professor Emeritus R. S., D.Sc., M.A. (*Fellow*).  
 JOHNSON, Mr. A. L., M.A.  
 KAMPS, Mr. F. J. H. (Belgium).  
 KEMP, Mr. J. F.  
 MORCOM, Mr. E. L., M.A.  
 PRIMROSE, Mr. H. S.  
 RADLEY, Mr. W. A., O.B.E.  
 ROBERTSON, Mr. W. H. A. (*Fellow*).  
 SCOTT, Mr. G. Shaw, M.Sc. (*Fellow*).

SELIGMAN, Dr. Richard (*Past-President and Fellow*).  
 SPITTLE, Mr. A.  
 WEBB, Mr. A. J., M.A., B.Sc.  
 WEIR OF EASTWOOD, The Right Hon. the Viscount, G.C.B., P.C., D.L., LL.D.

## OBITUARY

The Council records with regret the deaths of the following members : Mr. P. J. Ayckbourn; Mr. W. T. Bowen; Mr. R. W. Buzzard; Mr. M. C. Engers; M. Albert Féron (Original Member); Mr. J. R. Govett; Mr. G. W. Green; Mr. H. Hillier; Mr. J. E. Howard; Mr. P. V. Hunter; Dr. Henry Lepp; Mr. J. McNeil; Mr. E. N. Manchester; Mr. E. C. J. Marsh; Mr. W. M. Martin; Professor Dr. Georg Masing (Institute of Metals (Platinum) Medallist); Mr. W. G. Mochrie; Mr. F. Moulton; Mr. G. F. Mundell; Mr. J. H. Nead; Mr. R. P. J. Paul; Mr. J. S. Sarantis; Mr. E. Schutz; Dr. J. G. A. Skerl; Mr. R. E. L. Tricker, Mr. H. Vivian; Mr. R. Whitfield; and Mr. H. W. Williams (Original Member).

## OFFICERS OF THE INSTITUTE

The following members were declared elected to fill honorary offices of the Institute with effect from the 1956 Annual General Meeting :

*President :*

Major C. J. P. BALL, D.S.O., M.C., F.R.Ae.S.

*Past-President :*

MAURICE COOK, D.Sc., Ph.D., F.I.M.

*Vice-Presidents :*

N. P. INGLIS, Ph.D., M.Eng., M.I.Mech.E., F.I.M.  
 IVOR JENKINS, D.Sc., F.I.M.

*Ordinary Members of Council :*

G. L. BAILEY, C.B.E., M.Sc., F.I.M.  
 J. W. BERRY, M.I.Mech.E.  
 G. E. DOÑO, J.P.  
 H. M. FINNISTON, B.Sc., Ph.D., A.R.T.C., F.I.M.  
 Professor HUGH FORD, D.Sc., Ph.D., Wh.Sch., M.I.Mech.E.  
 C. H. M. HOLDEN, F.I.M.

In accordance with Article 42, the Council elected Dr. L. B. PFEIL, O.B.E., D.Sc., A.R.S.M., F.I.M., F.R.S., as Senior Vice-President for the year 1956-57.

## CORRESPONDING MEMBERS TO THE COUNCIL

The Council again desires to record its indebtedness to all the Corresponding Members for their services to the Institute, and for their advice, during the past year.

The following Corresponding Members retired during the year, their terms of office having been completed, and the Council expresses to them, on

behalf of the members, its warm thanks for the services they have rendered to the Institute: Dr. H. W. Worner (Australia); Professor G. Letendre (Canada); Professor L. Taverner (Union of South Africa); and Professor R. F. Mehl (United States of America).

Including new appointments, the Corresponding Members to the Council are now as follows: *Argentina*: Señor J. A. Sabato; *Australia*: Mr. C. Blazey and Professor H. K. Worner; *Austria*: Professor Dr. phil. E. Schmid; *Belgium*: Professor R. E. de Strycker; *Brazil*: Dr. L. C. Corrêa da Silva; *Canada*: Dr. G. S. Farnham, Professor F. A. Forward, and Mr. G. M. Young; *Chile*: Professor J. Païdassi; *Denmark*: Dr. B. Lunn; *Finland*: Professor H. M. Miekko-oja; *France*: Professor G. Chaudron and Dr. J. F. G. Hérenghuel; *Germany*: Professor Dr.-Ing. P. Brenner and Professor Dr. phil. W. Köster; *India*: Mr. G. C. Mitter and Professor D. Swarup; *Italy*: Dott. Aldo Daccò and Professor Dott. L. Matteoli; *Japan*: Professor Dr. I. Obinata; *Netherlands*: Professor Dr. W. G. Burgers; *Norway*: Professor A. B. Winterbottom; *South Africa*: Professor A. J. Gould; *Spain*: Señor F. Torras Serrataco; *Sweden*: Professor Dr. E. G. Rudberg; *Switzerland*: Dr. O. H. C. Messner; *United States of America*: Professor Morris Cohen; Dr. Kent R. Van Horn, and Dr. R. A. Wilkins.

#### INSTITUTE OF METALS MEDAL

The Institute of Metals (Platinum) Medal for 1956 was awarded to Professor GEORGES CHAUDRON, Dr.-ès Sc., Membre de l'Académie des Sciences, in recognition of his outstanding contributions to knowledge, particularly in the field of the light metals, which have greatly benefited the light-metal industries.

#### W. H. A. ROBERTSON MEDAL AND PREMIUM

The W. H. A. Robertson Medal for 1955, with a Premium of Fifty Guineas, was awarded to Mr. E. J. THACKWELL for a paper on "The Choice and Construction of Monolithic Linings for Twin-Bath Induction Furnaces for Melting Aluminium Alloys", which was published in the *Journal*, 1954-55, vol. 83, pp. 283-294.

#### ROSENHAIN MEDAL

The Rosenhain Medal for 1956 was awarded to Dr. DONALD McLEAN, in recognition of his outstanding contributions to knowledge in the field of physical metallurgy.

#### STUDENTS' ESSAY PRIZE

The Adjudicators awarded a prize of twenty-five guineas to Mr. M. DEIGHTON, B.Sc., for an essay on "A Consideration of the Changes and Mechanisms

Involved During the Annealing of Cold-Worked Metals". The essay was published in the *Bulletin*, 1956, vol. 3, pp. 93-96.

#### PUBLICATIONS

During the calendar year 1956, 73 papers and addresses were published in the *Journal* (for a list, see Appendix I to this report), comprising 598 pp. and 94 plates (compared with 511 pp. and 72 plates in 1955), and 624 pp. of *Metallurgical Abstracts* and annual indexes were printed (compared with 676 pp. in 1955). At the end of the year there were 53 unpublished MSS. in hand, compared with 41 at the end of the previous year.

In the *Monograph and Report Series*, further reprints were made of No. 1: "The Structure of Metals and Alloys", by Dr. W. Hume-Rothery and Professor G. V. Raynor, and No. 3: "Atomic Structure for Students of Metallurgy", by Dr. W. Hume-Rothery. A revision of No. 2: "The Constitutional Diagrams of Alloys: A Bibliography", by Mr. A. Prince, and the following new books of the series, were published: No. 17: "The Control of Quality in the Production of Wrought Non-Ferrous Metals. Part III.—The Control of Quality in Heat-Treatment and Final Operations", and No. 19: "The Running and Gating of Sand Castings: A Review of the Literature", by Mr. R. W. Ruddle. In addition, three books were sent to press, and were due to be published in January 1957, viz. No. 18: "The Mechanism of Phase Transformations in Metals"; No. 20: "The Final Forming and Shaping of Wrought Non-Ferrous Metals"; and No. 21: "The Foundations of Metallography", by Professor Dr. Georg Masing (translated from the German by Professor F. C. Thompson).

*Annotated Equilibrium Diagrams* were published of the systems aluminium-beryllium, aluminium-cobalt, aluminium-silver, aluminium-titanium (all by Mr. H. W. L. Phillips); antimony-tin (by Dr. E. C. Ellwood); copper-sulphur (by Dr. J. Nutting); chromium-iron, iron-manganese, iron-vanadium (each by Dr. A. Hellawell); magnesium-manganese and magnesium-zinc (both by Professor W. R. D. Jones).

The new quarterly periodical *Metallurgical Reviews* started publication. The issue of the first part was seriously delayed by a dispute in the printing industry, but the first three parts were published in 1956, and the last part of Volume I was sent to press during the year, and was due for despatch to subscribers in January 1957. Numerous reviews have been commissioned, and the Committee responsible for this new periodical expects that all issues of Volume II will be published and despatched in 1957.

The Council believes that *Metallurgical Reviews* meets a real need for authoritative, critical, and interpretative reviews of existing knowledge in various fields of metallurgical interest. The periodical covers the whole field of metallurgy, excepting mining, the



extraction of metals from their ores, and iron and steel works practice, and the contents include both industrial and theoretical subjects.

It is hoped that members will make widely known the publication of *Metallurgical Reviews*. This new venture deserves the support of all members and of numerous metallurgists throughout the world who, though they may not be members of the Institute, have need for reviews of the type issued.

#### GENERAL MEETINGS

On Friday, 24 February 1956, a General Meeting was held at the University, Edgbaston, Birmingham, when there was an Informal Discussion, arranged by the Metallurgical Engineering Committee, on "Refractories for Use in the Non-Ferrous Metals Industry". A brief report of this discussion was published in the *Bulletin*, 1956, vol. 3, pp. 115-116.

The Spring Meeting was held in London from Tuesday to Friday, 10-13 April 1956, the Annual May Lecture being delivered by Dr. Willis Jackson, F.R.S., on "Ferroelectrics—the Dielectric Analogue of Ferromagnetics". In connection with the meeting, the Metallurgical Engineering Committee arranged an all-day Symposium on "The Final Forming and Shaping of Wrought Non-Ferrous Metals", the Nuclear Energy Committee arranged a discussion and an exhibition of materials employed in nuclear-energy engineering, and Professor Dr. Erich Schmid delivered a lecture on "Electron Emission from Metals", by invitation of the Metal Physics Committee. The May Lecture and the papers discussed at the meeting have been published in the *Journal*.

The Metal Physics Committee arranged lectures in London on 25 April 1956 by Professor Cyril S. Smith on "The Beginnings of Metallography", and on 13 June 1956 by Professor R. Smoluchowski on "Some Recent Studies of Irradiation Effects in Metals and Other Solids".

The Autumn Meeting was held in Germany from Monday to Tuesday, 17-25 September 1956, by invitation of the Deutsche Gesellschaft für Metallkunde. After seven days in Stuttgart, the meeting concluded with two days at Frankfurt-am-Main, from which additional visits were paid to works and laboratories. The Autumn Lecture, delivered by Professor Dr. phil. W. Köster on "Some Metallurgical Advances: How and Why They Occurred", was published in the *Journal*. In connection with the meeting a Students' Tour was arranged.

On Monday and Tuesday, 3 and 4 December, a special General Meeting was held in London for the benefit of those members who were not able to attend the Autumn Meeting in Germany. Discussions took place on papers that had been published in the *Journal* and, in addition, under arrangements made by the Nuclear Energy Committee, Mr. L. Rotherham delivered a lecture on "Metallurgical Problems in the United Kingdom Atomic Energy Authority",

and, under the auspices of the Metal Physics Committee, Dr. A. H. Cottrell gave a report on some aspects of a conference recently held at Lake Placid, U.S.A., on "Dislocations and the Mechanical Properties of Crystals".

#### LOCAL SECTIONS AND ASSOCIATED SOCIETIES

Interesting programmes were arranged by the six Local Sections (Birmingham, London, Oxford, Scottish, Sheffield, and South Wales), the meetings of which were well attended.

As in previous years, members had the privilege of attending the meetings of the Associated Societies, viz. Leeds Metallurgical Society, Liverpool Metallurgical Society, Manchester Metallurgical Society, and North East Metallurgical Society.

The President (Dr. MAURICE COOK) was able to pay official visits to each of the Local Sections and Associated Societies during the 1955-56 winter session.

On Thursday, 6 December 1956, at Bristol, a joint meeting was held with the Bristol Section, Chemical Engineering Group, and Corrosion Group of the Society of Chemical Industry, at which papers were read on "Corrosion Fatigue", by Mr. T. D. Weaver and on "Stress Corrosion", by Dr. K. R. Wilson.

#### SPECIAL COMMITTEES

The Metal Physics Committee met twice in 1956. It arranged three lectures by visiting scientists, to which reference has been made above, and a session at the Spring Meeting on "Alloy Thermodynamics". Under the Committee's auspices, Dr. A. H. Cottrell gave a report on some aspects of the proceedings of a conference on "Dislocations and the Mechanical Properties of Crystals", held at Lake Placid, U.S.A., on 6-8 September 1956. The Committee is arranging a discussion on "The Metal Physics of Corrosion and Oxidation", to be held in connection with the 1957 Spring Meeting and an all-day Symposium on "Vacancies and Other Point Defects in Metals and Alloys", which will take place at Harwell in the winter of 1957. The Committee will welcome suggestions for ways in which it may be of help to the ordinary metallurgist.

The Metallurgical Engineering Committee held three meetings during the year. It arranged an Informal Discussion on "Refractories for Use in the Non-Ferrous Metals Industry" and an all-day Symposium on "The Final Forming and Shaping of Wrought Non-Ferrous Metals". The Committee has also planned an Informal Discussion on "Degreasing" and (in association with the Institute of British Foundrymen) an all-day Symposium on "Metallurgical Aspects of the Control of Quality in the Production of Non-Ferrous Castings" to be held in 1957, and invited certain papers on metallurgical engineering subjects for publication and subsequent discussion. The Council has approved a recom-

mendation of the Committee that, subject to support from the industry, instructional meetings, at suitable centres, should be held for younger members, at which papers on metallurgical engineering subjects would be read and discussed, and linked with visits to inspect certain aspects of industrial plant. These proposed meetings would be on lines very similar to those most successfully arranged in the iron and steel industry by the Engineers' Group of the Iron and Steel Institute.

The *Metallurgical Reviews* Committee met six times, and successfully launched the publication of this new quarterly periodical, to which reference has been made elsewhere in this report.

The Nuclear Energy Committee met three times. It arranged a discussion of papers on materials for nuclear power engineering and an exhibition in connection with the Spring Meeting and a lecture by Mr. L. Rotherham, to which reference has been made above. It has planned, in connection with the 1957 Spring Meeting, a session on the metallurgy of niobium, for which a series of six papers has been invited.

The work of the Publication Committee, which had six meetings, is referred to above in some detail under "Publications". The Committee has appointed a Sub-Committee to study whether economy in publication can be effected by devising a new form for the presentation of scientific papers.

#### STAFF

In a year of particularly great activity, due to the moving of our headquarters, all members of the staff have worked extremely well and have loyally responded to the heavy demands made upon them. The Council wishes to convey its appreciation and grateful thanks to each member.

The increase in volume of the Institute's publications has placed too great a burden on one Editor. In consequence, Mr. J. S. Bristow, B.Sc., F.I.M., was appointed Editor of *Metallurgical Abstracts* with effect from 9 April 1956, to relieve Mr. N. B. Vaughan, M.Sc., F.I.M., who remains Editor of the *Journal*, *Metallurgical Reviews*, the *Bulletin*, the books of the Monograph and Report Series, and the Annotated Equilibrium Diagram series.

#### JOINT ACTIVITIES

##### JOINT LIBRARY AND INFORMATION DEPARTMENT

During 1956, 12,690 \* publications were borrowed from the Joint Library (14,416 \* in 1955), and 401 new text-books were acquired (232 in 1955). Under certain conditions members can be supplied with photocopies or microfilms of documents, and during 1956 211 photocopies and 45 microfilms were prepared

(172 and 66 in 1955); of these about half of the photocopies and all the microfilms were sent overseas. The foregoing figures indicate the extent of the demands on the services of the Library, which come from Members, Government Departments, Universities, and Research Laboratories. From the same sources came a continuous flow of enquiries in a wide variety of fields; in dealing with these the Information Department seeks to supply answers by reference to the scientific and technical literature; it is careful not to encroach on the field of the metallurgical consultant.

During 1956, Imperial Chemical Industries, Ltd., through the Institute of Metals, made a third donation of £21 in appreciation of the services rendered to the Company by the Joint Library. Gillette Industries, Ltd., through The Iron and Steel Institute, presented to the Joint Library £105, in appreciation of services rendered to the Company. The money will be spent on something of use to the Library.

The Council thanks the Companies for these gifts, and all authors and others who have presented books, periodicals, or pamphlets to the Joint Library during the past year.

##### SIR GEORGE BEILBY MEMORIAL FUND

The Administrators of the Sir George Beilby Memorial Fund, representing the Institute of Metals, the Royal Institute of Chemistry, and the Society of Chemical Industry, made awards during the year of one hundred and fifty guineas each to:

F. D. RICHARDSON, B.Sc., Ph.D., in recognition of his work on the thermodynamic properties of high-temperature systems, with special reference to iron smelting and steel making.

F. WORMWELL, M.Sc., Ph.D., D.Sc., in recognition of his work on surface reactions, with special reference to the mechanism of corrosion, oxidation, and passivation processes.

##### JOINT COMMITTEE FOR NATIONAL CERTIFICATES IN METALLURGY

During the session 1955-56, the Joint Committee for National Certificates in Metallurgy approved two new schemes and eight revised schemes for the Higher National Certificate in Metallurgy; one new scheme and twelve revised schemes for the Ordinary National Certificate; and two new schemes for contributory centres.

There are thirty-eight Technical Colleges with courses approved for the Ordinary National Certificate in Metallurgy, and eleven contributory centres. Twenty-four Colleges have courses approved for the Higher National Certificate.

\* Loans to members of the staffs of The Institute of Metals and The Iron and Steel Institute are omitted from the figure for 1956; they amounted to 1210.



The results for 1955 and 1956 are given below :

Year	Technical Colleges	Number of Candidates			
		Entered	Total Awarded Certificates	With Distinction	With Prize Award
Ordinary National Certificate :					
1955	37	523	275	33	38
1956	37	571	296	31	42
Higher National Certificate :					
1955	21	183	138	22	30
1956	23	247	205	23	27
Endorsement Subjects—Ordinary National Certificate :					
1955	5	59	27	1	1
1956	6	56	23	7	7
Endorsement Subjects—Higher National Certificate :					
1955	11	70	66	7	7
1956	12	102	89	8	8
Assessed Examination in Mathematics S.2 :					
1955	23	487	284		
1956	28	570	391		

#### MOND NICKEL FELLOWSHIPS COMMITTEE

The Mond Nickel Fellowships Committee made the following awards in 1956 :

Mr. R. BANDY (The English Steel Tool Corporation, Ltd.) : to study, in the United Kingdom, Europe, and North America, metallurgical research, production methods, and quality control with respect to tool steels.

Dr. J. HARGREAVES (The United Steel Companies, Ltd.) : to study the changes in design, construction, and methods of operation of steel-making and processing furnaces which are being introduced in the United Kingdom, Europe, and the United States of America, to increase the rate and efficiency of production.

## APPENDIX I

## LIST OF PAPERS PUBLISHED

The following is a complete list of the papers and lectures published during the calendar year 1956

*In the Journal*

1664. On the Recrystallization of Cold-Rolled Commercially Pure Titanium. By Professor Ichiji Obinata, Dr.Eng., and Keizo Nishimura.
1665. The Intergranular Brittleness of Single-Phase Copper-Antimony Alloys. By L. M. T. Hopkin, Ph.D., A.R.S.M., A.I.M.
1666. Rotational Slip in Zinc Single Crystals. By A. D. Whapham, B.Sc., A.R.C.S.
1667. Plastic Laps for the Preparation of Specimens for Metallographic Examination. By V. J. Haddrell, E. C. Sykes, L.I.M., and B. W. Mott, M.A.
1668. Observations on the Mechanical Properties of Two Age-Hardenable Copper-Aluminium Alloys. By J. P. Dennison, B.Sc., Ph.D.
1669. A Miscibility Gap in the Face-Centred Cubic Phase of the Copper-Nickel-Chromium System. By Dr. J. L. Meijering, Professor Dr. G. W. Rathenau, M. G. van der Steeg, and P. B. Braun.
1670. The Machining Properties of Non-Ferrous Metals. By D. F. Galloway, Ph.D., Wh.Sch., M.I.Mech.E., M.I.Prod.E., M.I.I.A., A.M.I.E.E., B.Sc.Hons., M.Inst.Pet.
1671. The Deep Drawing and Spinning of Sheet Metal, with Particular Reference to Non-Ferrous Materials. By John A. Grainger, A.M.I.Mech.E., A.M.I.Prod.E., A.M.I.I.A.
1672. Rubber Pressing. By J. Fielding, A.M.I.Mech.E., Assoc.M.C.T.(Met.).
1673. The Manufacture and Properties of High-Strength Nickel-Tungsten Alloys. By M. Davis, B.Sc., Ph.D., A.Inst.P., C. E. Densem, B.Sc.Tech., and J. H. Rendall, B.Sc., A.R.S.M., A.I.M.
1674. Research into Some Metal-Forming and Shaping Operations. By W. Johnson, B.Sc.Tech., B.Sc., A.M.I.Mech.E.
1675. Cold Roll-Forming and Manipulation of Light-Gauge Sections. By E. Griffin, A.M.I.Mech.E., A.M.I.Prod.E.
1676. Stretch-Forming of Non-Ferrous Metals. By R. D. Edwards, A.M.I.Mech.E.
1677. Bending and Allied Forming Operations. By T. G. Perry, B.A., S.M.
1678. The Hot Forming of Magnesium Alloys. By R. G. Wilkinson, B.Sc.
1679. Metallurgical Research and Development for Nuclear Power. By H. K. Hardy, D.Sc., Ph.D., A.R.S.M., A.I.M.
1680. Metallurgical Research in Nuclear Power Production. By J. G. Ball, B.Sc., F.I.M.
1681. Selection of Canning Materials for Reactors Cooled by Sodium/Potassium and Carbon Dioxide. By A. B. McIntosh, Ph.D., B.Sc., F.R.I.C., A.R.T.C., F.I.M., and K. Q. Bagley, Ph.D., B.Sc.
1682. New and Improved Metallurgical Techniques. 26th Autumn Lecture. By C. Sykes, D.Sc., Ph.D., F.R.S.
1683. Some Metallographic Observations on the Fatigue Failure of Bare and Clad Aluminium-Copper-Magnesium Alloy Sheet. By J. J. Sebesty, B.Sc., and J. O. Edwards, M.Sc.
1684. A Graphical Solution of the Cold-Rolling Problem, When Tensions are Applied to the Strip. By G. Lianis, Dipl.Ing., D.I.C., and Professor Hugh Ford, D.Sc., Ph.D.
1685. The Constitution of the Titanium-Tin System in the Region 0-25 Atomic Per Cent. Tin. By (Mrs.) M. K. McQuillan, M.A.
1686. The Constitutional Diagram of the System Chromium-Beryllium from 0 to 70 Atomic Per Cent. Beryllium. By A. R. Edwards, B.Met.E., and S. T. M. Johnstone, B.Met.E., A.I.M.
1687. Slip-Band Extrusion. By E. A. Calnan, Ph.D., and Betty E. Williams.
1688. Experiments on the Semi-Continuous Casting of Bronze. By E. C. Ellwood, Ph.D., M.I.M.M., F.I.M., J. C. Prytherch, M.Sc., Ph.D., F.I.M., and E. F. Phelps.
1689. The Porosity and Permeability of Hot-Compacted Copper Powder. By G. Arthur, B.Sc., Ph.D., A.R.T.C.
1690. The Solid Solubilities of Tin, Indium, and Cadmium in Aluminium. By L. E. Samuels, B.Met.E., M.Sc., A.I.M.
1691. The Criterion for the Cleavage Fracture of Zinc Single Crystals. By A. Deruytère, Ph.D., and G. B. Greenough, M.A., Ph.D.
1692. The Lattice Spacings of Nickel-Copper and Palladium-Silver Alloys. By B. R. Coles, B.Sc., D.Phil.
1693. A Note on the Plotting of Accurate Large-Scale Stereographic Projections. By J. W. Christian, M.A., D.Phil.
1694. The Influence of Mould Variables and Inhibitors on Mould Reaction in Aluminium-10% Magnesium Alloy. By Marjorie Whitaker, B.Sc., A.I.M. With an Appendix on The Effect of Moulding and Casting Variables on Mould Reaction in Aluminium-5% Magnesium Alloy. By J. Lund, B.A.Sc.
1695. Structural Changes During the Fatigue of Some Aluminium Alloys. By T. Broom, M.A., Ph.D., J. H. Molineux, M.Sc., and V. N. Whittaker, B.Sc.
1696. The Mechanical Properties of Binary and Ternary Magnesium Alloys Containing Lithium. By Professor W. R. D. Jones, D.Sc.
1697. The Structure and Growth of Oxide Layers Formed on Beryllium. By I. S. Kerr, Ph.D., and H. Wilman, D.Sc., Ph.D., F.Inst.P.
1698. Applications of the Phenomenological Theories of Martensite. I.—Geometrical Treatment. II.—Related Types of Martensitic Transformation. By J. W. Christian, M.A., D.Phil.
1699. The History of Magnesium. Presidential Address. By Major C. J. P. Ball, D.S.O., M.C., F.R.Ae.S.
1700. The Stress-Corrosion of Certain Aluminium Alloys. By H. K. Farmery, M.A., Ph.D., and U. R. Evans, Sc.D., F.R.S.
1701. The Phase Sections at 500° and 350° C. of Aluminium-Rich Aluminium-Copper-Lithium Alloys. By H. K. Hardy, D.Sc., Ph.D., A.R.S.M., A.I.M., and (Miss) J. M. Silcock, B.Sc.
1702. Trace-Element Effects in Some Precipitation-Hardening Aluminium Alloys. By H. K. Hardy, D.Sc., Ph.D., A.R.S.M., A.I.M.
1703. The Dissociation Pressures in the Zirconium-Oxygen System at 1000° C. By O. Kubaschewski, Dr.phil.habil., and W. A. Dench.
1704. The Routine Determination of the Hydrogen Content of Aluminium and Aluminium Alloys by the Hot-Extraction Method. By C. E. Ransley, Ph.D., F.I.M., and D. E. J. Talbot, M.Sc.
1705. A Recording Camera for Metallography with Polarized Light. By B. R. Butcher, B.Sc., and I. A. McDonald, F.I.M., and D. E. J. Talbot, M.Sc.
1706. Ferroelectrics: The Dielectric Analogue of Ferromagnetics. 46th Annual May Lecture. By Willis Jackson, D.Sc., D.Phil., M.I.E.E., F.R.S.
1707. Decomposition of the Beta Phase in a Copper-Gallium Eutectoid Alloy. By Chester W. Spencer, Ph.D., and Associate Professor David J. Mack, Ph.D.
1708. The Cleavage Fracture of Copper-Plated Zinc Single Crystals. By G. B. Greenough, M.A., Ph.D., and D. A. Ryder, A.I.M.
1709. Electron-Microscopic Observations on the Precipitation of the  $\theta'$  Phase in an Aluminium-4% Copper Alloy. By E. Langer, M.Sc.



1710. Sub-Structure Formation in Slightly Bent Aluminium Single Crystals. By H. J. Lambot, Dr.Sc.
1711. The Plastic Deformation of Aluminium and Aluminium Alloys. By G. Thomas, B.Sc., Ph.D., and J. Nutting, M.A., B.Sc., Ph.D.
1712. The Refinement of Cast Grain-Size in Copper-Aluminium Alloys Containing 7-9 Per Cent. Aluminium. By J. P. Dennison, B.Sc., Ph.D., and E. V. Tull, B.Sc., M.Sc., A.I.M.
1713. Some Observations on the Development of Face-Centred Cubic Rolling Textures. By R. F. Braybrook, B.A., and E. A. Calnan, Ph.D.
1714. Observations on Grain-Boundary Migration in Aluminium Bicrystals. By K. T. Aust, (Mrs.) E. H. Harrison, and Professor R. Maddin.
1715. The Attack of Unstressed Metals by Liquid Mercury. By J. F. Strachan, B.Sc., B.Sc.(Eng.), A.M.I.E.E., A.Inst.P., and N. L. Harris, B.Sc., F.Inst.P.
1716. The Effect of High and Low Temperatures on the Notched-Bar Characteristics of a Cast, High-Tensile, Beta-Brass. By A. R. Bailey, M.Sc., A.I.M., R. McDonald, L.I.M., and L. E. Samuels, B.Met.E., M.Sc., A.I.M.
1717. The Constitution of Tin-Indium Alloys in the Range 0-30 Per Cent. Indium. By J. C. Blade, Ph.D., and E. C. Ellwood, Ph.D., M.I.M.M., F.I.M.
1718. The Removal of Oxide from Aluminium by Brazing Fluxes. By M. F. Jordan, B.Sc., Ph.D., and D. R. Milner, M.Sc.
1719. The Relation During Creep Between Grain-Boundary Sliding, Sub-Crystal Size, and Extension. By D. McLean, D.Sc., and M. H. Farmer, B.Sc.
1720. The Nature of Mechanically Polished Metal Surfaces: The Surface Deformation Produced by the Abrasion and Polishing of 70:30 Brass. By L. E. Samuels, B.Met.E., M.Sc., A.I.M.
1721. The System Uranium-Palladium. By J. A. Catterall, Ph.D., D.I.C., A.R.S.M., J. D. Grogan, B.A., and R. J. Pleasance.
1722. Some Experiments on the Determination of the Latent Heats of Transition of Titanium and Iron. By T. H. Schofield, M.Sc., F.I.M.
1723. The Behaviour of Interfaces in Lightly Worked Uranium During Recrystallization. By P. E. Madsen, B.Sc.
1724. Calculation of the Contribution Made by Grain-Boundary Sliding to Total Tensile Elongation. By H. Brunner, Mech.Eng., and Professor N. J. Grant, Sc.D.
1725. The Effects of Internal Oxidation on the Tensile Properties of Some Silver Alloys at Room and Elevated Temperatures. By E. Gregory, M.A., Ph.D., and G. C. Smith, M.A.
1726. A Study of the Hydrogen-Pressure Relationships in the Zirconium-Hydrogen System. By C. E. Ells, M.A., and A. D. McQuillan, B.Sc., Ph.D.
1727. The Constitution of Copper-Rich Alloys of the Copper-Manganese-Aluminium System. By D. R. F. West, Ph.D., B.Sc., D.I.C., A.I.M., and D. Lloyd Thomas, B.Sc.
1728. The Hardness of Manganese and Some Manganese-Rich Alloys. By Vernon Griffiths, M.Sc., Sc.D., and H. O'Neill, D.Sc., M.Met.
1729. Lattice Spacings of the Silver-Rich Solid Solution Containing Magnesium and Antimony. By R. B. Hill, M.Sc., Ph.D., and H. J. Axon, D.Phil.
1730. Some Metallurgical Advances: How and Why They Occurred. 27th Autumn Lecture. By Professor Dr. Werner Köster.
1731. The Equilibrium Diagram of the System Copper-Germanium. By J. Reynolds, B.A., and W. Hume-Rothery, O.B.E., F.R.S.
1732. Pseudo-Subgrain Structures on Aluminium Surfaces. By N. C. Welsh, B.Sc., Ph.D.
1733. Flow and Fracture Characteristics of Binary Wrought Magnesium-Lithium Alloys. By M. W. Toaz, M.Sc., and E. J. Ripling, Ph.D.
1734. Solution-Rate Studies with Liquid Metals: Solution of Copper in Liquid Lead and Bismuth. By A. G. Ward, L.I.M., and J. W. Taylor, Ph.D.
1735. Effects of Cyclic Stress and Frequency on Deformation Markings in Fatigued Copper. By D. S. Kemsley, M.Sc., F.M.T.C.
1736. The Cold-Rolled Texture of Hafnium. By Professor D. S. Eppelsheimer, D.Sc., and D. S. Gould, M.S.

*In the Bulletin*

- B13. A Consideration of the Changes and Mechanisms Involved During the Annealing of Cold-Worked Metals. By M. Deighton, B.Sc.
- B14. Radiation Damage to Metals and Associated Problems. The Effect of Neutron Irradiation on the Mechanical Properties of Metals. By M. J. Makin, B.Sc., Ph.D. Radiation Damage in Ionic Solids. By J. H. O. Varley, B.Sc., Ph.D. Changes in the Properties of Uranium During Burn-Up. By S. F. Pugh, M.A., A.I.M.
- Metallographic Methods for Highly Active Specimens. By P. C. L. Pfeil, Ph.D., B.Sc.
- B15. Refractories for Use in the Non-Ferrous Metals Industry. (Informal Discussion.)
- B16. Radiation Damage to Metals and Associated Problems (concl.). Irradiation Techniques for Fissile Materials. By O. S. Plail.

## APPENDIX II

CONTRIBUTIONS TO THE INDUSTRIAL DONATIONS FUND IN, OR FOR, THE FINANCIAL YEAR ENDED 30 JUNE 1956

Donor	Gross, after Recovery of Tax by the Institute	Donor	Gross, after Recovery of Tax by the Institute
	£ s. d.		£ s. d.
*Enfield Rolling Mills, Ltd. (incl. Enfield Copper Refining Co., Ltd.; Enfield Rolling Mills (Aluminium), Ltd.; Holloway Metal Roofs, Ltd.; and London Zinc Mills, Ltd.)	478 5 3	Rylands Brothers, Ltd.	100 0 0
*Mond Nickel Co., Ltd., The (incl. Henry Wiggin and Co., Ltd., and associated companies in the United States and Canada)	478 5 3	*Manganese Bronze and Brass Co., Ltd., The	†91 6 1
*Consolidated Zinc Corporation, Ltd., The (incl. The Broken Hill Corporation, Ltd.; Imperial Smelting Corporation, Ltd.; The National Smelting Co., Ltd.; New Broken Hill Consolidated, Ltd.; Northern Smelting and Chemical Co., Ltd.; Sulphide Corporation Ltd.; and The Zinc Corporation, Ltd.)	434 15 8	General Electric Co. (U.S.A.), \$250	89 12 0
*Goodlass Wall and Lead Industries, Ltd.; Associated Lead Industries, Ltd.	£173 18 3	*Aluminium Wire and Cable Co., Ltd.	86 19 2
Fry's Metal Foundries, Ltd. (incl. The Antifriction Bearing Co., Ltd.; Atlas Metal and Alloys, Ltd.; and The Eyre Smelting Co., Ltd.)	£86 19 2	*Consolidated Tin Smelters, Ltd. (incl. The Cornish Tin Smelting Co., Ltd.; Eastern Smelting Co., Ltd.; The Penpoll Tin Smelting Co., Ltd.; and Williams, Harvey and Co., Ltd.)	86 19 2
*Mufulira Copper Mines, Ltd.	260 17 5	*Enthoven (H. J.) and Sons, Ltd.	86 19 2
*Roan Antelope Copper Mines, Ltd.	260 17 5	*High Duty Alloys, Ltd.	86 19 2
*Imperial Chemical Industries, Ltd., and its subsidiary companies	250 0 0	*Rolls-Royce, Ltd.	86 19 2
Aluminium Laboratories, Ltd. (incl. Aluminium Union, Ltd.; Northern Aluminium Co., Ltd.; and Aluminium (Canada), Ltd.)	200 0 0	*Stone (J.) and Co. (Charlton), Ltd.	86 19 2
General Motors, Ltd. (incl. A.C. Sphinx Spark Plug Co., Ltd.; Delco-Remy-Hyatt, Ltd.; and Frigidaire, Ltd.)	200 0 0	*Venesta, Ltd.	86 19 2
Tube Investments, Ltd. (incl. The Chesterfield Tube Co., Ltd.; Mersey Cable Works, Ltd.; Reynolds Light Alloys, Ltd.; Reynolds Rolling Mills, Ltd.; Simplex Electric Co., Ltd.; South Wales Aluminium Co., Ltd.; and T.I. Aluminium, Ltd.)	200 0 0	*Whiley (Geo. M.), Ltd.	86 19 2
*Metallo-Chemical Refining Co., Ltd.	181 16 4	Mallory Metallurgical Products, Ltd.	52 10 0
*British Aluminium Co., Ltd., The (incl. Aluminium Corporation, Ltd.; William Mills, Ltd.; and North British Aluminium Co., Ltd.)	173 18 3	Pyrotenax, Ltd.	52 10 0
*McKechnie Brothers, Ltd.	173 18 3	*Associated Electrical Industries, Ltd., on behalf of the A.E.I. Group of Companies	50 0 0
*Magnesium Elektron, Ltd. (incl. F. A. Hughes and Co., Ltd.)	173 18 3	Austin Motor Co., Ltd.	50 0 0
Nchanga Consolidated Copper Mines, Ltd.	150 0 0	Birmingham Small Arms Co., Ltd., on behalf of the B.S.A. Group of Companies	50 0 0
Rhodesia Broken Hill Development Co., Ltd., The	150 0 0	*Dale (John), Ltd.	50 0 0
Rhokana Corporation, Ltd.	150 0 0	Davy and United Engineering Co., Ltd.	50 0 0
Vickers Group of Companies: Vickers-Armstrongs (Aircraft), Ltd.; Vickers-Armstrongs (Shipbuilders), Ltd.; English Steel Corporation Ltd., and Vickers, Ltd. (incl. A.B.C. Motors, Ltd.; Robert Boby, Ltd.; Cooke, Troughton and Simms, Ltd.; Ioco, Ltd.; George Mann and Co., Ltd.; Onions and Sons (Levellers) Ltd.; Palmers Hebburn Co., Ltd.; and Powers-Samas Accounting Machines, Ltd.)	105 0 0	Lucas (Joseph), Ltd. (incl. Rotax, Ltd.)	50 0 0
Booth (James) and Co., Ltd.	100 0 0	Morris Motors, Ltd.	50 0 0
Copper Pass and Son, Ltd. (incl. George Pizey and Co., Ltd.; The Tyne Solder Co., and Victor G. Stevens, Ltd.)	100 0 0	*Tennant (C.), Sons and Co., Ltd.	†50 0 0
Colvilles, Ltd.	100 0 0	*Murex, Ltd. (incl. Murex Welding Processes, Ltd.)	47 16 6
Johnson (Richard) and Nephew, Ltd.	100 0 0	*Morgan Crucible Co., Ltd.	46 3 0
Johnson, Matthey and Co., Ltd.	100 0 0	*Simon-Carves, Ltd.	45 13 0
		*Hopkinsons, Ltd.	45 4 4
		*A.P.V. Co., Ltd.	43 9 6
		*Birmetals, Ltd.	43 9 6
		*Birmingham Aluminium Casting (1903) Co., Ltd.	43 9 6
		*Bristol Aeroplane Co., Ltd., The	43 9 6
		*British Metal Corporation, Ltd., The	43 9 6
		*Chloride Electrical Storage Co., Ltd., The	43 9 6
		*London and Scandinavian Metallurgical Co., Ltd.	43 9 6
		*Rotol, Ltd.	43 9 6
		*Star Aluminium Co., Ltd. (incl. Anglo-Swiss Aluminium Co., Ltd.)	43 9 6
		*Sterling Metals, Ltd.	43 9 6
		*Telegraph Construction and Maintenance Co., Ltd., The (incl. Submarine Cables, Ltd.)	43 9 6
		*Wolverhampton Metal Co., Ltd., The (incl. James Bridge Copper Works, Ltd.)	43 9 6
		Wednesbury Tube Co., Ltd., The	42 0 0
		*Hughes-Johnson Stampings, Ltd., The	36 10 5
		*Light Metal Forgings, Ltd.	36 10 5
		*Ferranti, Ltd.	34 15 9
		*Gibbons Brothers, Ltd. (incl. The Thermic Equipment and Engineering Co., Ltd.)	34 15 9
		*Parkinson Stove Co., Ltd., The	†34 15 9
		*British Tin Investment Corporation, Ltd.	27 7 10
		*Derby and Co., Ltd.	27 7 10
		*London Electric Wire Company and Smiths, Ltd., The (incl. Liverpool Electric Cable Co., Ltd.)	†27 7 0
		English Electric Co., Ltd., The (incl. D. Napier and Son, Ltd.)	26 5 0
		Head, Wrightson and Co., Ltd.	26 5 0
		Metal Box Co., Ltd., The	26 5 0
		*Barker and Allen, Ltd.	26 1 9
		*Bolton (Thomas) and Sons, Ltd.	26 1 9
		*British Lead Mills, Ltd.	26 1 9
		*Perry Barr Metal Co., Ltd.	26 1 9
		Arkinstall Brothers, Ltd.	25 0 0



Donor	Gross, after Recovery of Tax by the Institute		
	£	s.	d.
Birmingham Battery and Metal Co., Ltd.	25	0	0
Braby (Frederick) and Co., Ltd.	25	0	0
British Timken, Ltd. (incl. Fischer Bearings Co., Ltd.)	25	0	0
British United Shoe Machinery Co., Ltd., The	25	0	0
Fairey Aviation Co., Ltd., The	25	0	0
Gardner (Henry) and Co., Ltd.	25	0	0
Messina Transvaal Development Co., Ltd., The	25	0	0
Plessey Co., Ltd., The	25	0	0
Pressed Steel Co., Ltd.	25	0	0
Roe (A. V.) and Co., Ltd.	25	0	0
Thompson (John) (Wolverhampton), Ltd.	25	0	0
*Holroyd (John) and Co., Ltd.	23	18	3
Bull's Metal and Marine Co., Ltd.	21	0	0
Delta Metal Co., Ltd., The (incl. Heaton and Dugard, Ltd.)	21	0	0
Fulmer Research Institute, Ltd.	21	0	0
Leigh and Silavan, Ltd.	21	0	0
Monotype Corporation, Ltd., The	21	0	0
Newey and Tayler, Ltd. (incl. Newey Brothers, Ltd., and D. F. Tayler and Co., Ltd.)	21	0	0
Philips Electrical, Ltd.	21	0	0
*International Alloys, Ltd.	20	19	0
Brightside Foundry and Engineering Co., Ltd., The	20	0	0
Deloro Stellite, Ltd.	20	0	0
Hall and Pickles, Ltd.	20	0	0
Hard Metal Tools, Ltd.	20	0	0
Park Gate Iron and Steel Co., Ltd., The	20	0	0
Sheffield Smelting Co., Ltd.	20	0	0
*Allen (Edgar) and Co., Ltd.	18	5	2
*British Tin Smelting Co., Ltd., The	18	5	2
*General Electric Co., Ltd., The	18	5	2
*Phosphor Bronze Co., Ltd., The	18	5	2
*Saunders-Roe, Ltd.	18	5	2
*Wolverhampton Die-Casting Co., Ltd., The	18	3	7
*Chase Non-Ferrous Metal Co., Ltd.	17	7	9
*Curran (Edward) Engineering, Ltd.	17	7	9
*Rollet (H.) and Co., Ltd.	17	7	9
Marconi's Wireless Telegraph Co., Ltd.	15	15	0
*Loewy Engineering Co., Ltd., The	13	0	10
Brotherhood (Peter), Ltd.	12	12	0
Carborundum Co., Ltd., The	10	10	0
Clifford (Charles) and Son, Ltd.	10	10	0
Copper and Alloys, Ltd.	10	10	0
Foundry Services, Ltd.	10	10	0
Fry's Diecastings, Ltd.	10	10	0
Glynn Brothers, Ltd.	10	10	0
G.W.B. Electric Furnaces, Ltd.	10	10	0
Harrison (Birmingham), Ltd.	10	10	0
Hills (West Bromwich), Ltd.	10	10	0
Hoover, Ltd.	10	10	0
Incandescent Heat Co., Ltd., The (incl. Controlled Heat and Air, Ltd.; Metal Porcelains, Ltd.; Metaelectric Furnaces, Ltd.; and Selas Gas and Engineering Co., Ltd.)	10	10	0
Strebor Diecasting Co., Ltd.	10	10	0

Donor	Gross, after Recovery of Tax by the Institute		
	£	s.	d.
Vauxhall Motors, Ltd.	10	10	0
West Yorkshire Foundries, Ltd.	10	10	0
Allen (W. H.), Sons and Co., Ltd.	10	0	0
Electric Furnace Co., Ltd. (incl. Electro-Chemical Engineering Co., Ltd.)	10	0	0
Electric Resistance Furnace Co., Ltd.	10	0	0
Elliott Brothers (London), Ltd.	10	0	0
Highton and Son, Ltd.	10	0	0
Metro-Cutanit, Ltd.	10	0	0
Rothschild (N. M.) and Sons	10	0	0
*North Thames Gas Board	9	19	3
*Central Marine Engine Works (William Gray and Co., Ltd.)	9	2	6
*Corfield-Sigg, Ltd.	9	2	6
*Harland Engineering Co., Ltd., The	9	2	6
*Maudslay Motor Co., Ltd., The	9	2	6
*Wild-Barfield Electric Furnaces, Ltd.	9	2	6
*Winfields Rolling Mills, Ltd.	9	2	6
*Bound Brook Bearings (G.B.), Ltd.	8	14	0
*Hoyt Metal Company of Great Britain, Ltd., The	8	14	0
*Hunt and Mitton, Ltd.	8	14	0
*Jenkinson (W. G.), Ltd.	8	14	0
*Shaw, Son and Greenhalgh, Ltd.	8	14	0
*Stein (John G.) and Co., Ltd.	8	14	0
*Betts and Co., Ltd.	7	6	1
*Glenfield and Kennedy, Ltd.	7	0	6
United Wire Works (Birmingham), Ltd.	6	6	0
Acton Bolt, Ltd.	5	5	0
Beryllium and Copper Alloys, Ltd.	5	5	0
Blackwells Metallurgical Works, Ltd.	5	5	0
Dennison Watch Case Co., Ltd.	5	5	0
Easdale (R. M.) and Co.	5	5	0
Headlley, Birch and Co., Ltd.	5	5	0
Lead Wool Co., Ltd., The	5	5	0
Miles (John) and Partners (London), Ltd.	5	5	0
Ratcliffs (Great Bridge), Ltd.	5	5	0
Rigby (John) and Sons, Ltd.	5	5	0
Wilkinson (John) and Sons (Saltley), Ltd.	5	5	0
Cambridge Instrument Co., Ltd., The	5	0	0
Electro-Alloys, Ltd.	5	0	0
Langley Alloys, Ltd.	5	0	0
Rubery, Owen and Co., Ltd.	4	10	6
Blakeborough (J.) and Sons, Ltd.	4	4	0
Kincaid (John G.) and Co., Ltd.	4	4	0
*Tungum Co., Ltd., The	†3	11	0
*Acorn Anodising Co., Ltd.	†3	9	6
*Platt Metals, Ltd.	3	9	6
Metal Information Bureau, Ltd.	3	3	0
Mining and Chemical Products, Ltd.	3	3	0
Carobronze, Ltd.	2	2	0
Follsain-Wycliffe Foundries, Ltd.	2	2	0
Gascoignes Non-Ferrous Foundries, Ltd.	2	2	0
Premier Cooler and Engineering Co., Ltd., The	2	2	0
Sheffield Testing Works, Ltd., The	2	2	0
Metal Supplies, Ltd.	2	0	0
Jenks (E. P.), Ltd.	1	1	0

\* Annual Donation, Under Covenant, for Not Less than 7 Years.

† Includes tax recoverable, but not actually recovered in the financial year 1955-56.

## APPENDIX III

## COMMITTEES

The main committees of the Institute which have served during the year were constituted as follows at 31 December 1956 :

## FINANCE AND GENERAL PURPOSES COMMITTEE

HAMER, Mr. R. D. (*Chairman*).  
 COOK, Dr. Maurice.  
 DOREY, Dr. S. F.  
 GRIMSTON, The Hon. John.  
 JONES, Mr. E. H.  
 THOMAS, Mr. W. J.  
 THOMPSON, Professor F. C.

*Ex-officio :*

BALL, Major C. J. P. (*President*).  
 PFEIL, Dr. L. B. (*Senior Vice-President*).  
 COLQUHOUN, Mr. J. C. (*Honorary Treasurer*).  
 TEED, Major P. Litherland (*Chairman, Publication Committee*).

## HOUSE COMMITTEE

COOK, Dr. Maurice (*Chairman*).  
 COLQUHOUN, Mr. J. C.  
 PFEIL, Dr. L. B.

*Ex-officio :*

BALL, Major C. J. P. (*President*).  
 HAMER, Mr. R. D. (*Chairman, Finance and General Purposes Committee*).

## LIBRARY COMMITTEE

CHASTON, Dr. J. C. (*Chairman*).  
 CHILTON, Mr. L. V.  
 FULLMAN, Mr. B.

GUILLAN, Lieut.-Colonel S. C.  
 PARKER, Miss E. W.

## LOCAL SECTIONS COMMITTEE

PFEIL, Dr. L. B. (*Chairman*).  
 ASHTON, Mr. A. B.  
 GARSIDE, Dr. J. E.  
 KENNETT, Dr. S. J.

*Ex-officio :*

BALL, Major C. J. P. (*President*).  
 PFEIL, Dr. L. B. (*Senior Vice-President*).  
 COLQUHOUN, Mr. J. C. (*Honorary Treasurer*).  
 HIGNETT, Mr. H. W. G. (*Chairman, Birmingham Local Section*).  
 MATTHEWS, Mr. A. W. (*Honorary Secretary, Birmingham Local Section*).  
 RHODES, Dr. E. C. (*Chairman, London Local Section*).  
 KNIGHT, Mr. J. R. (*Honorary Secretary, London Local Section*).

MURRAY, Mr. G. (*Chairman, Oxford Local Section*).  
 PEARCE, Mr. R. (*Honorary Secretary, Oxford Local Section*).  
 DUNLOP, Mr. W. A. (*Chairman, Scottish Local Section*).  
 HAY, Mr. Matthew (*Honorary Secretary, Scottish Local Section*).  
 EDWARDS, Dr. A. (*Chairman, Sheffield Local Section*).  
 MACDOUGALL, Mr. A. J. (*Honorary Secretary, Sheffield Local Section*).  
 O'NEILL, Professor H. (*Chairman, South Wales Local Section*).  
 DENNISON, Dr. J. P. (*Honorary Secretary, South Wales Local Section*).

## METAL PHYSICS COMMITTEE

O'NEILL, Professor H. (*Chairman*).  
 AXON, Dr. H. J.  
 BAILEY, Dr. G. L. J.  
 CHRISTIAN, Dr. J. W.  
 FINNISTON, Dr. H. M.  
 FORSYTH, Mr. P. J. E.  
 FRANK, Professor F. C.  
 GEACH, Dr. G. A.  
 HANSTOCK, Dr. R. F.  
 KING, Dr. Ronald.  
 NUTTING, Dr. J.  
 OLIVER, Mr. D. A. (representing the Iron and Steel Institute and the British Iron and Steel Research Association).

RICHARDS, Dr. T. Ll.  
 RICHARDSON, Dr. F. D.  
 WAKEMAN, Dr. D. W.

*Ex-officio :*

BALL, Major C. J. P. (*President*).  
 TEED, Major P. L. (*Chairman, Publication Committee*).

## METALLURGICAL ENGINEERING COMMITTEE

FORD, Professor H. (*Chairman*).  
 ASHTON, Mr. A. B.  
 BAKER, Dr. W. A.  
 BOLTON, Mr. E. A.  
 BOND-WILLIAMS, Mr. N. I.  
 BOWMAN, Mr. W. H.  
 CLARKE, Mr. D. H. H.  
 DAVIES, Mr. C. E.  
 LAKE, Mr. N. C.  
 MORTON, Mr. J. S.  
 PATON, Mr. C. P.

SALTER, Mr. J.  
 SINGER, Professor A. R. E.  
 WALTON, Mr. J. S.  
 WILKINSON, Mr. R. G.

*Ex-officio :*

BALL, Major C. J. P. (*President*).  
 TEED, Major P. L. (*Chairman, Publication Committee*).

## "METALLURGICAL REVIEWS" COMMITTEE

JENKINS, Dr. Ivor (*Chairman*).  
 BAKER, Dr. W. A.  
 CHASTON, Dr. J. C.  
 FORD, Professor H.  
 GADD, Mr. E. R.  
 HOAR, Dr. T. P.  
 NORTHCOTT, Dr. L. (representing the Institution of Metallurgists).  
 RAYNOR, Professor G. V.  
 SALTER, Mr. J.

SCHUEER, Dr. E.  
 SMITH, Mr. S. S.

*Ex-officio :*

BALL, Major C. J. P. (*President*).  
 HAMER, Mr. R. D. (*Chairman, Finance and General Purposes Committee*).  
 COLQUHOUN, Mr. J. C. (*Honorary Treasurer*).

## NUCLEAR ENERGY COMMITTEE

BAILEY, Mr. G. L. (*Chairman*).  
 BURWOOD, Mr. D. S.  
 COLBECK, Mr. E. W.  
 COOK, Dr. Maurice.  
 FINNISTON, Dr. H. M.  
 HOPKIN, Mr. G. L.  
 JENKINS, Dr. Ivor.  
 MILLER, Dr. G. L.  
 QUARRELL, Professor A. G.

ROTHERHAM, Mr. L.  
 SMITH, Mr. S. S.  
 SMITHELLS, Dr. C. J.

*Ex-officio :*

BALL, Major C. J. P. (*President*).  
 TEED, Major P. L. (*Chairman, Publication Committee*).

## PUBLICATION COMMITTEE

TEED, Major P. L. (*Chairman*).  
 BAKER, Dr. W. A.  
 CHRISTIAN, Dr. J. W.  
 CROWTHER, Mr. J.  
 CUTHBERTSON, Professor J. W.  
 FINNISTON, Dr. H. M.  
 FRENCH, Mr. A. R.  
 JENKINS, Dr. Ivor.  
 KEE, Mr. W. W.  
 KING, Dr. Ronald.  
 MAKOWER, Mr. A.  
 PARKER, Dr. R. T.  
 PFEIL, Dr. L. B. (representing Local Sections Committee).  
 PHILLIPS, Mr. H. W. L.  
 POWELL, Mr. A. R.  
 SHOWELL, Mr. D. W. D.

SMITH, Mr. S. S.  
 WALTERS, Mr. B.

*Ex-officio :*

BALL, Major C. J. P. (*President*).  
 HAMER, Mr. R. D. (*Chairman, Finance and General Purposes Committee*).  
 COLQUHOUN, Mr. J. C. (*Honorary Treasurer*).  
 O'NEILL, Professor H. (*Chairman, Metal Physics Committee*).  
 FORD, Professor H. (*Chairman, Metallurgical Engineering Committee*).

## MEDAL COMMITTEE

PRESIDENT (*Chairman*).  
 SENIOR VICE-PRESIDENT.

and

Not more than four Institute of Metals (Platinum) Medal

lists who are, or have been, members of the Council (to be selected by the President), with power to the President to co-opt not more than two other persons.

## NOMINATIONS COMMITTEE

PRESIDENT (*Chairman*).  
 TWO IMMEDIATE PAST-PRESIDENTS.

SENIOR VICE-PRESIDENT.

## STAFF COMMITTEE

CHAIRMAN, FINANCE AND GENERAL PURPOSES COMMITTEE (*Chairman*).

HONORARY TREASURER.



# REPORT OF THE HONORARY TREASURER

## FOR THE FINANCIAL YEAR ENDED 30 JUNE 1956

THERE was an excess of normal income over normal expenditure for the year of £1343, as compared with a deficit in the previous year of £575. In all the circumstances, this is regarded as very satisfactory, bearing in mind the continual expansion of the Institute's membership and activities and the rising costs affecting so many of the items of administrative and publishing expenditure.

The normal Income and Expenditure Account shows a net increase of income of £3457. There were increases in membership subscriptions (£1483), sales of the *Journal* and *Metallurgical Abstracts* (£3353), and interest on investments (£225), and decreases in income from Industrial Donations (£964), advertisements (£423), and sales of Special Publications (£264).

On the expenditure side, the principal increases were in establishment expenses (£642), administration and production expenses (£1511), superannuation (£909), joint activities (£622), and production costs of Special Publications (£445).

During the year, new agreements were reached with the Iron and Steel Institute regarding rent and services for office accommodation at 4 Grosvenor Gardens, and for library services. The full effect of increases arising from the new agreements was not felt in the financial year under review, but they involved additional expenditure of £418 in the case of rent and services and £375 for the Joint Library. The full year's increase for rent and services at 4 Grosvenor Gardens will not now be felt, of course, because of the Institute's move to its new Head-

quarters, but in the next financial year the cost of the library services will have risen from £500 in 1954-55 to £1000 per annum.

Below the usual Income and Expenditure Account there are shown, separately, items of income and expenditure relating principally to the acquisition of the lease of the Institute's headquarters. In order to finance this transaction, the Council decided to sell some of its General Fund investments, which realized £9978, and made arrangements with its bankers for a loan of £15,000 on the security of its investments, other than those of the Endowment Fund. As it was a term of its undertaking to Industry that its investments in the Endowment Fund should not be sold, it will be obvious that (a) in order to meet the loss of interest on the investments sold and interest on the overdraft and (b) to find the cash to pay off the overdraft, the Institute must rely on the continuation of donations by members and Industry at least equal to those of recent years.

The Balance Sheet requires little comment. Cash at £22,495 represented a temporary accumulation from donations and investments sold in anticipation of expenditure early in the new financial year. Net Current Assets are temporarily swollen for the same reason, and there has since been a big increase in Fixed Assets at the expense of these two items.

In regard to the selection of investments, the arrangements continue under which the banking firm of Morgan Grenfell & Co., Ltd., act for the Institute in an advisory capacity.

## THE INSTITUTE OF METALS

[illegible]

## REPORT TO THE MEMBERS OF THE INSTITUTE OF METALS

We have audited the above Balance Sheet dated 30 June 1956, and the annexed Income and Expenditure Account for the year ended 30 June 1956, and report that we have obtained all the information and explanations which to the best of our knowledge and belief were necessary for the purposes of our audit.

In our opinion proper books of account have been kept by the Institute so far as appears from our examination of those books. The above-mentioned Balance Sheet and annexed Income and Expenditure Account are in agreement with the Books of Account. In our opinion, and to the best of the information and according to the explanations given us, the said Accounts give the information required by the Companies Act 1946, in the manner so required, and give a true and fair view, in the case of the Balance Sheet of the state of the Institute's affairs as at 30 June 1956, and in the case of the Income and Expenditure Account of the excess of Income over Expenditure for the year ended 30 June 1956.

Approved on behalf of the Council: C. J. P. BALL, *President*.  
J. C. COLQUHOUN, *Honorary Treasurer*.

R. D. HAMER, *Chairman, Finance and General Purposes Committee.*  
S. C. GUILLAN, *Secretary.*

POPPLETON AND APPLEBY,  
CHARTERED ACCOUNTANTS, BIRMINGHAM  
20 December 1956.



# THE INSTITUTE OF METALS INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 30 JUNE, 1956

1955	£	1955	£	1955	£	1955	£
ESTABLISHMENT EXPENSES				MEMBERS' SUBSCRIPTIONS AND DONATIONS			
Rent, Rates, Services and Insurance	1,041		1,459	INDUSTRIAL DONATIONS			17,183
Lighting and Heating	280		251	INTEREST ON INVESTMENTS			8,484
Repairs and Renewals	108		361	General Funds	556		1,030
	1,429		2,071	Endowment Fund	769		764
ADMINISTRATION AND PRODUCTION EXPENSES				Industrial Donations Fund	244		
Salaries, Wages, and National Insurance	11,407		12,055		1,569		1,704
Postage, Despatch, and Telephone	733		990				
Sundry Expenses (including Bank Charges)	403		511				
Printing and Stationery (less Stocks)	647		887				
Audit Fee	105		105				
Professional Charges	273		314				
Staff Travelling and Secretarial Expenses	534		621				
Council and Committee Expenses	181		76				
	14,048		15,559				
SUPERANNUATION AND PENSIONS TO FORMER STAFF	2,367		3,376				
METINGS AND LOCAL SECTIONS, ETC.							
Meeting Expenses (net)	1,161		570				
Local Sections and Associated and Allied Societies	641		875				
Prizes and Medals	49		24				
	1,851		1,469				
JOINT ACTIVITIES							
Official Entertaining	67		294				
Joint Library Contribution	500		875				
Subscriptions to Joint Committees and Other Bodies and Presentations	163		188				
	735		1,357				
JOINT METALLURGICAL SOCIETIES MEETING IN EUROPE	1,157						
BAD DEBTS AND DOUBTFUL SUBSCRIPTIONS	238		141				
DEPRECIATION: FURNITURE AND EQUIPMENT	164		298				
LIST OF MEMBERS	178		52				
SPECIAL DEVELOPMENT WORK			90				
	22,207		24,313				
PUBLICATIONS (excluding Salaries and Overheads included above)							
Journal and Metallurgical Abstracts	21,092		21,997				
Ten Year Index to Metallurgical Abstracts	1,189						
Special Publications	2,564		3,009				
Miscellaneous Publications			172				
	25,745		25,178				
EXPENDITURE FOR YEAR (see Costing Allocation Below)	47,952		49,491				
EXCESS OF INCOME OVER EXPENDITURE FOR THE YEAR			1,343				
	£47,952		£50,834				
EXCESS OF EXPENDITURE OVER INCOME	575						
REMOVAL EXPENSES	41		124				
LOSS ON SALE OF INVESTMENTS			2,056				
TRANSFER TO ACCUMULATED SURPLUS			12,127				
	£976		£14,307				

EXCESS OF INCOME OVER EXPENDITURE FOR THE YEAR	1,343
SPECIAL DONATIONS	12,964
TRANSFER TO INDUSTRIAL DONATIONS FUND	
	£14,307

The Costing of the Activities of the Institute for the Year is as follows:

Publications:	
Journal and Metallurgical Abstracts	37,947
Special Publications	6,548
Activities other than Publications	4,956
	£47,952

# THE INSTITUTE OF METALS FUND ACCOUNTS FOR THE YEAR ENDED 30 JUNE, 1956

## INSTITUTE FUND

### ENDOWMENT FUND

	1955	1956
Transfer to General Funds: Investment Interest	£ 769	£ 764
Balance at 30 June 1956	21,297	21,295
		Interest on investments and bank interest
		771
		£ 766
		£22,063
		£22,066

## FUNDS ADMINISTERED BY THE INSTITUTE

### MOND NICKEL FELLOWSHIPS FUND

	1955	1956
Grants to Fellows, including travelling	£ 2,639	£ 5,781
Printing, stationery, postage and publicity	190	134
Bank charges	3	3
Secretarial expenses	260	250
Legal charges re trust deed	72	—
Balance at 30 June 1956:	16,800	11,800
Securities, per schedule	6,457	5,765
Cash at bank	231	319
Debtors and accrued interest	23,488	17,884
		£24,051
		£26,642

### CAPPER PASS FUND

	1955	1956
Grants	£ 760	£ 741
Balance at 30 June 1956: Cash at bank and interest thereon accrued due	—	19
		Bank interest
		£773
		£760

## SCHEDULE OF SECURITIES, 30 JUNE 1956

### GENERAL FUNDS

	1955	1956	At Cost unless otherwise stated	Market Value
I.D.F.	£	£	£	£
1,000 Consett Iron Co., Ltd., Ordinary Shares	1,217	—	1,286	1,100
£200 The "Shell" Transport and Trading Co., Ltd., Ordinary Stock	1,100	—	1,217	1,844
400 The General Electric Co., Ltd., Ordinary Stock	2,500	—	1,100	1,075
£1,500 British Electricity Authority 4½% Guaranteed Stock, 1967/69	3,000	—	1,477	1,393
£2,500 3½% Savings Bonds, 1960/70	1,010	—	2,500	1,919
£3,000 3½% Savings Bonds, 1965/75	162	—	3,000	2,227
£1,010 2½% Treasury Stock	—	—	1,010	628
150 £1 W. Savings Certificates, at Cost plus accrued interest to 22.11.50	—	—	162	175
950 £250 3½% Funding Stock, 1966/68	—	—	950	748
871 £500 Guest Keen and Nettlefolds, Ltd., Ordinary Stock	2,030	—	871	1,125
£2,000 British Transport 4½% Guaranteed Stock	1,358	—	2,030	1,698
500 Distillers Co., Ltd., Ordinary Shares	—	—	646	612
£1,500 British Electricity Authority 3½% Guaranteed Stock	5,563	—	1,338	1,172
£1,500 Consolidated Stock	2,659	—	—	—
2½% National War Bonds	1,000	—	—	—
4% Funding Stock	—	—	—	—
	£17,251	£11,819	£17,587	£15,516
	£	£	£	£
£1,285 3½% Savings Bonds	1,285	—	1,285	986
£17,926 5s. 1d. 4½% Consolidated Stock	19,482	—	19,482	13,871
£534 1s. 8d. British Electricity Authority 4½% Guaranteed Stock	—	—	527	496
	£20,767	—	£21,294	£15,353
	£	£	£	£
Woolwich Equitable Building Society	10,550	—	10,550	10,550
Co-operative Permanent Building Society	1,250	—	1,250	1,250
Abbey National Building Society	6,000	—	—	—
	£16,800	—	£11,800	£11,800

### MOND NICKEL FELLOWSHIPS FUND





FIG. 23.—Section Through a Large Sand Casting in Aluminium-4½% Copper Alloy Showing Coarse Grain-Size due to Gravity Segregation in Freezing. Etched in 100 parts HNO<sub>3</sub>, 50 parts HCl, 15 parts HF. × 1.



FIG. 11.—Macrostructures of the Bars in Fig. 12, Showing the Effect of Mode of Solidification on Properties. Fairly satisfactory results were recorded for the upper and centre bars, which had a columnar structure, while the equiaxed lower bar gave a very poor result.

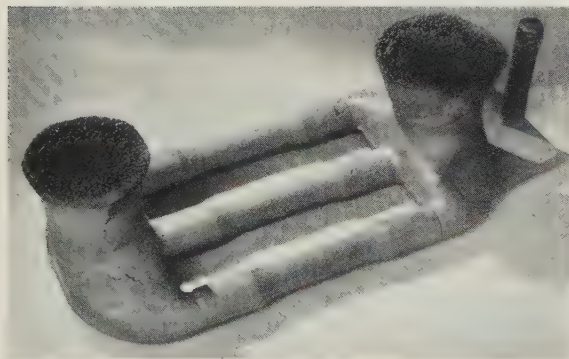


FIG. 12.—Set of Three Leaded Gun-Metal Bars Cast Together.

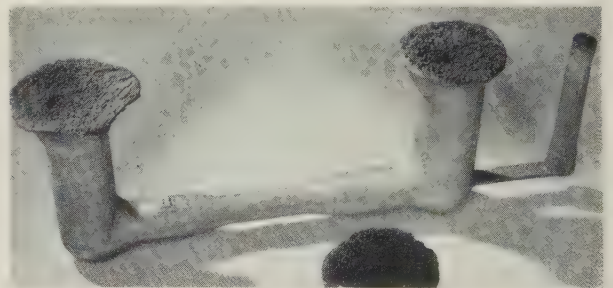


FIG. 13.—One of a Set of Three Leaded Gun-Metal Bars Cast Separately.



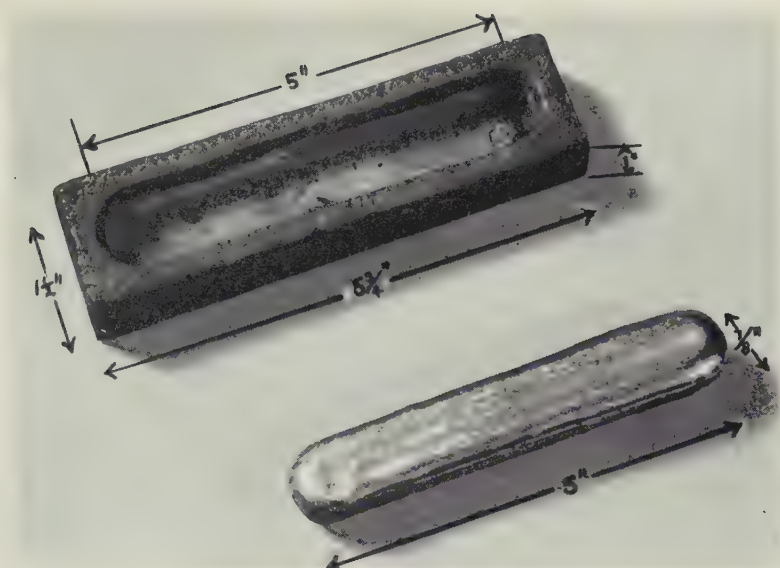
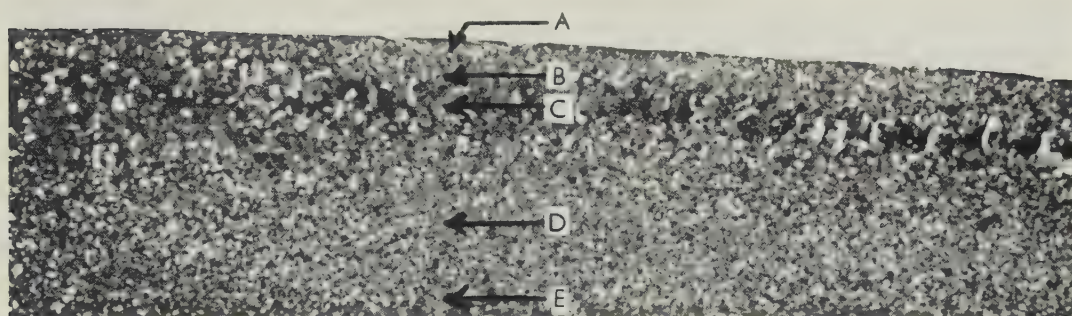
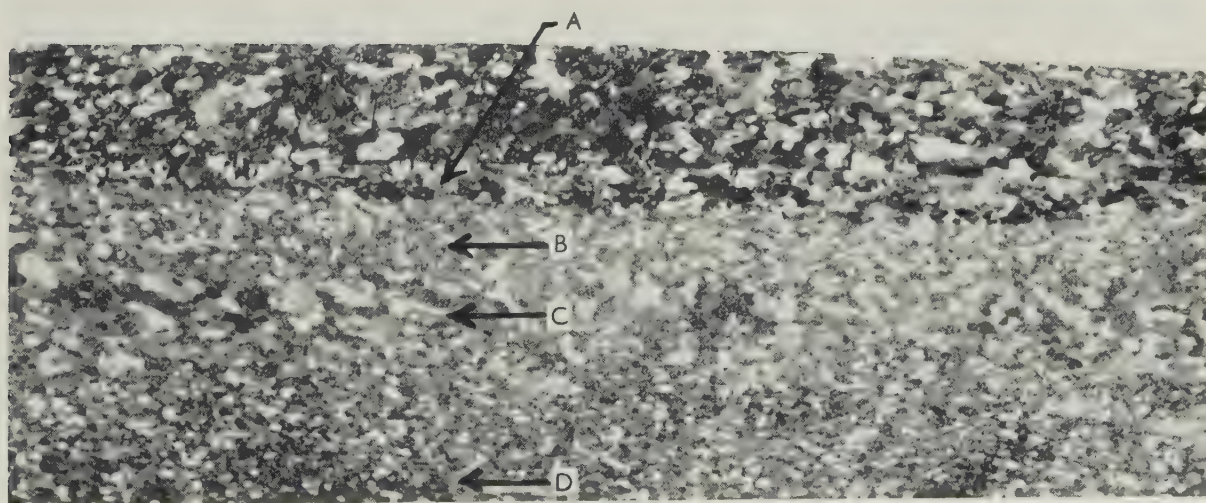


FIG. 14.—Bar and Mould Used in the Fracture-Bar Test.



(a)



(b)

FIG. 15.—Illustrating Normal Coarse-Grained Zone and Abnormal Inverse Segregate Formed in Cast Copper Alloys Under Certain Conditions of Solidification (see text, p. 313). (a) Shows a complete section and (b) the upper portion and top surface of the section, both photographed the way up as cast. Specimens for chemical analysis were taken at the points indicated and the results are given in Table IX (p. 313). (a)  $\times \frac{8}{5}$ ; (b)  $\times 1$  approx.



FIG. 16.—Photomicrograph of Casting Illustrated in Fig. 15, Showing that While the General Structure of the Casting is  $\alpha/\beta$ , the Structure of the Inverse Segregate is  $\beta$  and  $\beta/\gamma$ .  $\times 50$ .  
(Reduced by  $\frac{1}{3}$  in reproduction.)



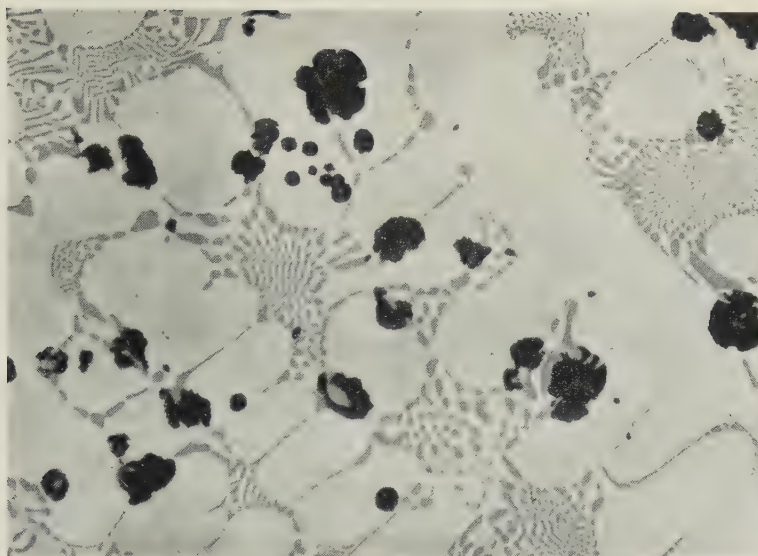


FIG. 12.—A Nickel-Carbon Alloy Containing Magnesium and Showing Nodular Graphite.  $\times 200$ .

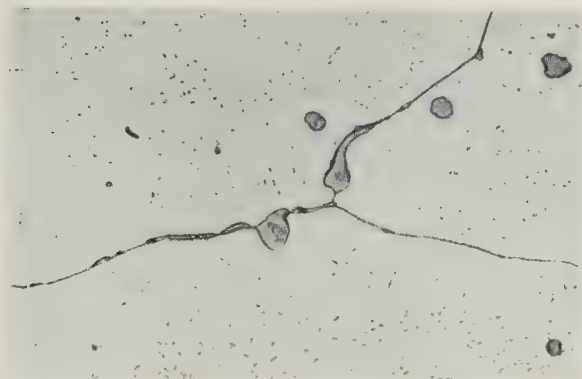
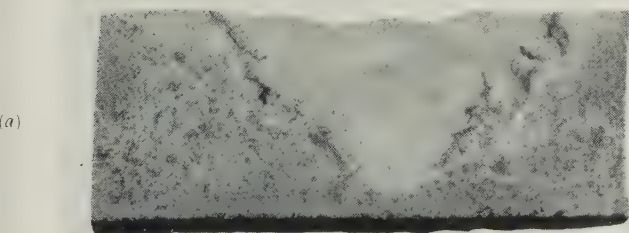


FIG. 13.—Cast Monel Containing 0.053% Sulphur and No Magnesium. (*Eash and Kihlgren*.<sup>4</sup>)  $\times 250$ .



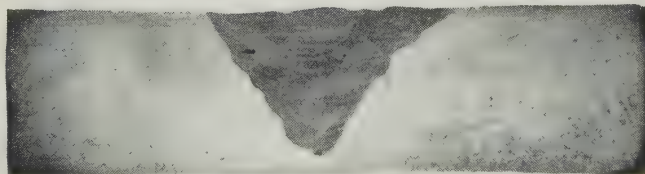
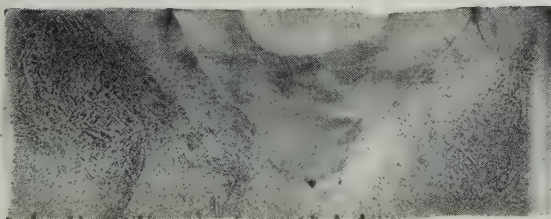
FIG. 14.—Cast Monel Containing 0.089% Sulphur and 0.09% Magnesium. (*Eash and Kihlgren*.<sup>4</sup>)  $\times 250$ .



(a)

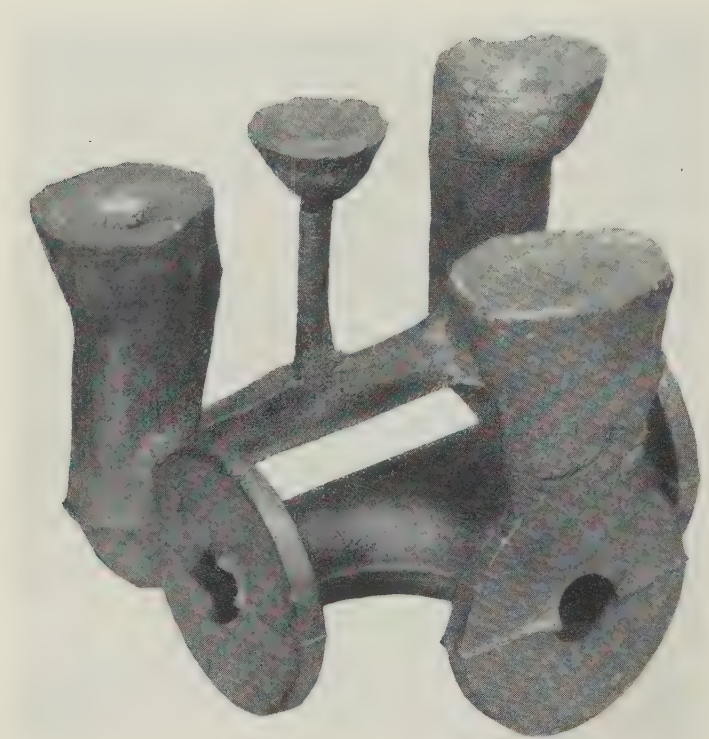


(b)



(d)

FIG. 15.—Transverse Sections of Welded Monel Castings Made from : (a) Ordinary Monel Pig; (b) Monel Pig Containing 1% Niobium; (c) Monel Pig Containing 2% Niobium; (d) Oxygen-Lanced Monel Pig. Sections etched in acidified cuprous chloride solution.  $\times 1$ .



[Courtesy Phosphor Bronze Co., Ltd.]

FIG. 16.—Method of Running and Feeding a Monel Pipe-Connection Casting.  $\times \frac{1}{2}$ .



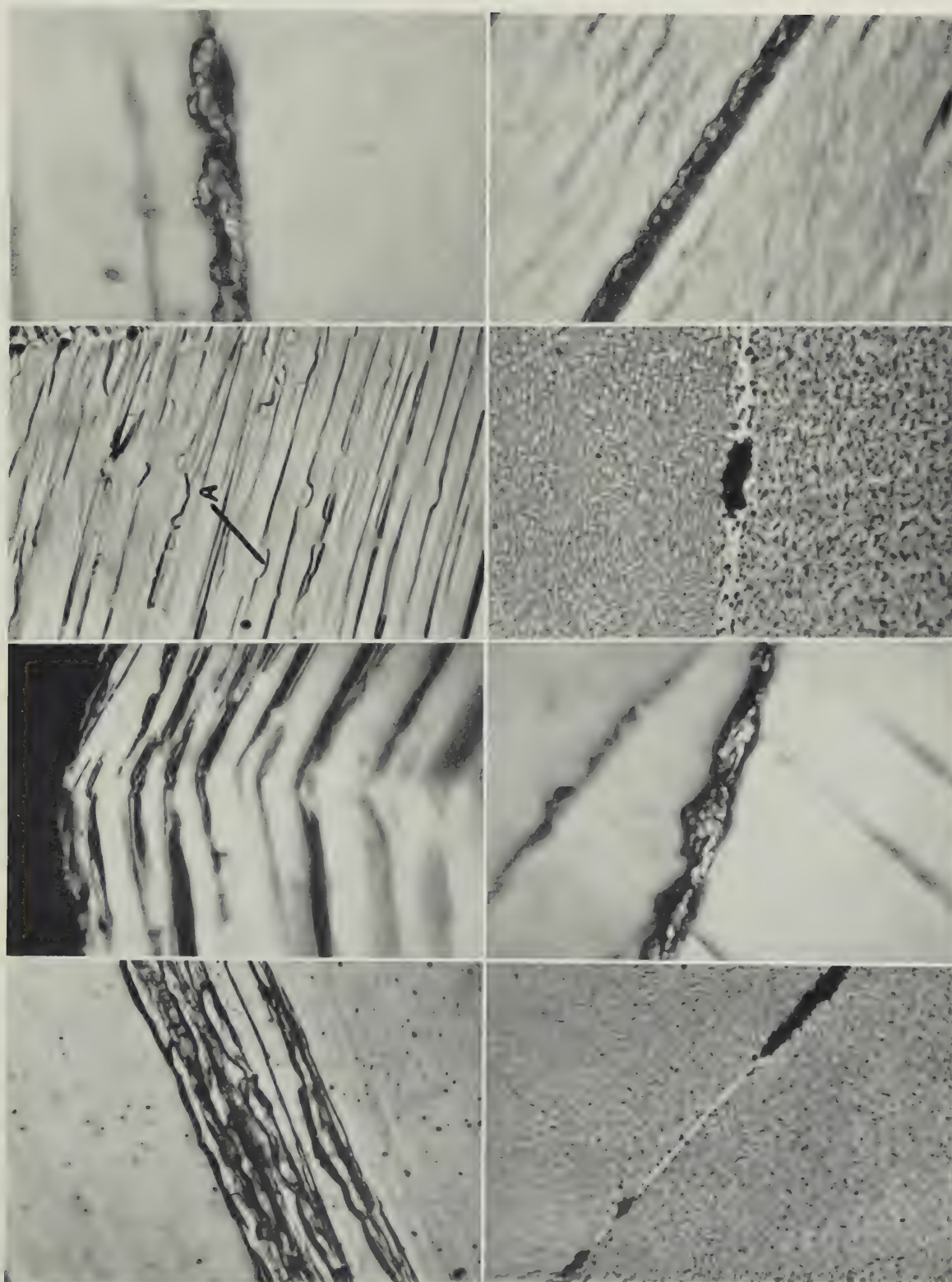
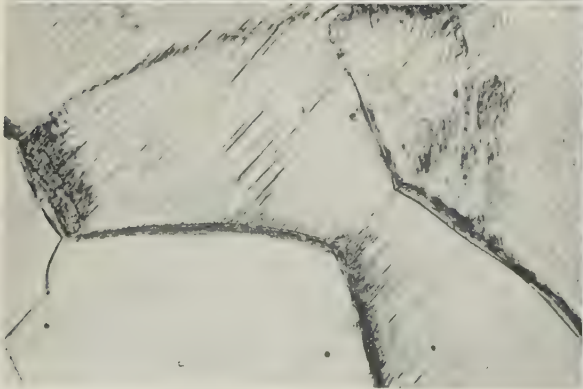


FIG. 1.—4% Cu, 0.05% Sn, Fatigued at Room Temperature.  
 FIG. 2.—3.1% Cu, 1.5% Mg, Fatigued at 195° C. in Solution Treated Condition.  
 FIG. 3.—4% Cu, 0.05% Sn, Fatigued at 195° C. in Solution Treated Condition.  
 FIG. 4.—4% Cu, Fatigued at 250° C., Showing Thick Slip-Band Extrusion.  
 FIG. 5.—4% Cu, Fatigued at 250° C. and Repolished to Show Depleted Slip Zones  
 FIG. 6.—4% Cu, Fatigued at 250° C., Showing Eruption at a Grain-Boundary.  
 FIG. 7.—4% Cu, Fatigued at 250° C. and Repolished to Show Copper Depletion at a Grain Boundary.  
 FIG. 8.—10% Zn, Fatigued at 100° C., Showing Eruption Along a Slip Band.

FIG. 1.—4% Cu, 0.05% Sn, Fatigued at Room Temperature.  
 FIG. 2.—3.1% Cu, 1.5% Mg, Fatigued at 195° C. in Solution Treated Condition.  
 FIG. 3.—4% Cu, 0.05% Sn, Fatigued at 195° C. in Solution Treated Condition.  
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 FIG. 6.—4% Cu, Fatigued at 250° C., Showing Eruption at a Grain-Boundary.  
 FIG. 7.—4% Cu, Fatigued at 250° C. and Repolished to Show Copper Depletion at a Grain Boundary.  
 FIG. 8.—10% Zn, Fatigued at 100° C., Showing Eruption Along a Slip Band.

FATIGUE EFFECTS IN ALUMINIUM ALLOYS.

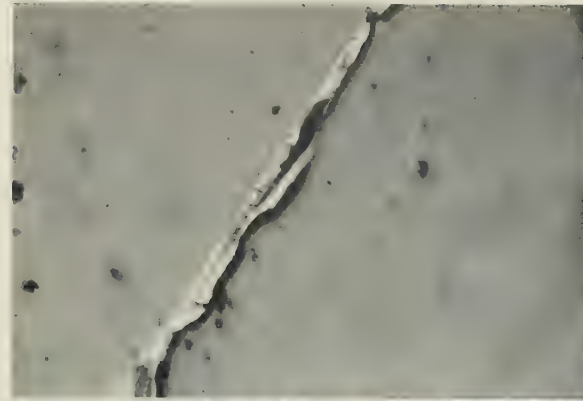
9



10



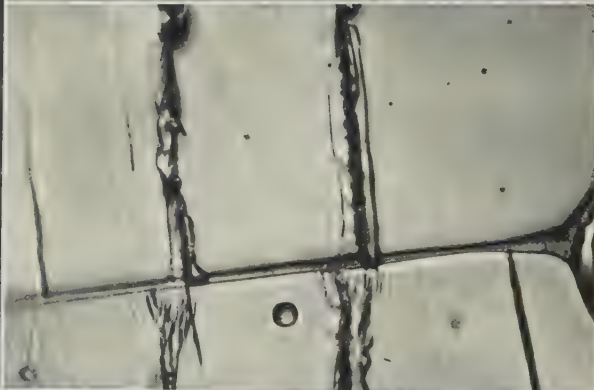
11



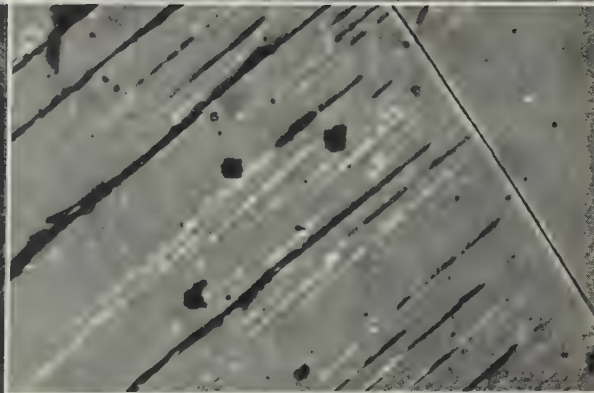
12



13



14



15

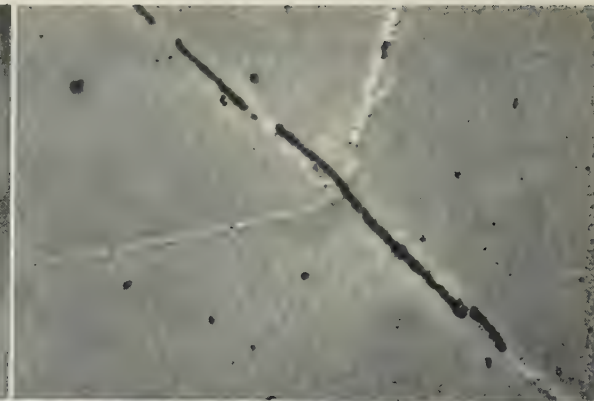


FIG. 9.—10% Zn, Fatigued at 150° C., Showing Boundary Deformation.  $\times 250$ .  
FIG. 10.—4% Cu, Fatigued at 250° C.  $\times 90$ .  
FIG. 11.—4% Cu, Fatigued at 200° C. and Then at Room Temperature.  $\times 1500$ .  
FIG. 12.—4% Cu, Fatigued at 200° C. and Subsequently Statically Stressed.  $\times 1000$ .  
FIG. 14.—4% Cu, Fatigued at Room Temperature and Subsequently Aged without Repolishing.  $\times 1500$ .  
FIG. 15.—4% Cu, Fatigued at 250° C., Showing Depleted Zone Dependent on Stress Concentration.  $\times 750$ .



# NON-DESTRUCTIVE TESTING IN THE CONTROL OF QUALITY OF NON-FERROUS CASTINGS \*

1754

By S. L. FRY †

## SYNOPSIS

After brief reference has been made to methods such as visual inspection, liquid penetration, pressure testing, ultrasonic testing, and fluoroscopy, the main part of the paper is devoted to a discussion of the radiographic examination of castings, and to the interpretation of the results. Defects detectable in radiographs are illustrated.

## I.—INTRODUCTION

THE availability of non-destructive methods of testing has resulted in recent years in a considerable increase in the field of application of castings, and their present-day use for highly stressed components depends on the fact that individual castings can be critically examined.

The methods of non-destructive testing suitable for use with castings are: (a) visual inspection, (b) liquid-penetration methods, (c) pressure testing, (d) ultrasonic testing, and (e) radiographic examination. It is proposed to deal only very briefly with the first four of these, which have frequently been described in the literature,‡ and then to concentrate on radiographic inspection, which is the method capable of giving the greatest range of information.

## II.—VISUAL INSPECTION

A great deal can be learnt from the careful visual examination of a casting both before and after fettling. Among defects that are readily seen on first inspection are gross shrinkage, misruns, severe turbulence, sand holes, and scabs. Closer examination may reveal cold shuts, blows, cracks, sinks, local burning, and direction of flow.

Visual inspection should always be carried out before embarking on other methods of non-destructive testing, for in this way a guide may be obtained to the parts of the casting that will most repay examination.

## III.—LIQUID PENETRATION METHODS

Penetration methods depend on the introduction of a suitable liquid containing a dye into the pores and cracks of a casting by immersing it in the liquid for a time. The surplus dye is then removed, and this is an important part of the process. Incomplete removal gives too much background, which tends to obscure the indications, whilst too severe washing will dilute the dye in the crack to such an extent that no evidence remains. The casting is then allowed to stand and the seepage of the liquid reveals the location of the cracks.

Greater sensitivity is obtained by the use of a developer, fine white powder which is either dusted or sprayed on to the casting. The powder draws the dye from the voids and also collects it at the point of the defect, thus showing faults in a more definite manner.

The penetrant can either be a brightly coloured dye or a fluorescent material; in the latter case it shows up under a source of ultra-violet rays.

In the case of a crack, a thin, continuous line of liquid or a series of tiny drops will gradually become visible; porosity or microshrinkage appears as individual spots or as areas covered with dye. The time required varies with the size of the defect; a fine crack may take up to 24 hr. to become apparent.

Castings must be well cleaned before they are subjected to the liquid-penetration method of test, and it is essential that they be degreased if they have been previously oil-quenched.

## IV.—PRESSURE TESTING

This form of test is very searching and is essential for castings that are to be used for certain applications. If a casting is found to lack pressure-tightness, other methods of testing must be used to determine the nature and location of the defects in it. The method of test is simple. All possible exits are blocked in the casting and air, oil, or water admitted under pressure. If any leaks show, the areas are suitably marked.

## V.—ULTRASONIC TESTING

Although ultrasonics are extensively used for inspecting cast billets, which are simple in shape, the method has not yet been developed for shaped castings. It is possible, however, that techniques for this purpose will be evolved. If so, they are likely to lead to a reduction in the number of castings radiographed.

## VI.—FLUOROSCOPY

In this method—which is applicable only to light-alloy castings—radiation from an X-ray tube passes through the casting under examination and then falls on a fluores-

\* Manuscript received 4 October 1956. Contribution to a Symposium on "Metallurgical Aspects of the Control of Quality in Non-Ferrous Castings" to be held in London on 1 May 1957.

† Chief Radiologist, J. Stone and Co. (Charlton), Ltd., London.  
‡ See, for example, "The Non-Destructive Testing of Metals", by R. F. Hanstock. 1951: London (Institute of Metals).

cent screen, where it excites an image of the casting that can be directly observed in a darkened room. The image is approximately natural size, but by using a source of small focal area, a useful degree of enlargement can be obtained.

Screening a casting in this way enables a very rapid examination to be made, and the method has the advantage that the position of the casting can be altered while it is actually being examined. Moreover, the cost of film, which makes radiography expensive, is avoided. On the other hand, screening is capable of revealing only gross defects, and general porosity would have to be unusually severe to be detected by this method.

## VII.—RADIOGRAPHY

### 1. GENERAL CONSIDERATIONS

Radiographic examination is at present the most important method of non-destructive testing of castings, as it yields more information than any other method about the type, size, and location of internal defects.

It is not proposed to discuss here X-ray apparatus, the properties of X-rays, the principles of radiography, or the precautions necessary to avoid dangers to health arising from exposure to X-rays. All these are dealt with in numerous text-books.\* Rather it is proposed to describe and illustrate the various defects that can be found in castings by radiography.

Numerous types of X-ray set are available, ranging normally from 50 to 1000 kV. The voltage applied to the X-ray tube controls the wave-length of the radiation emitted and hence its penetrating power. A rough guide to the penetration is given in Table I. The figures quoted are based on an exposure time of 57 m.amp.sec. on medium-contrast film and 225 m.amp.sec. on high-contrast film at a film-focal spot distance of 40 in. The developing time for the film is 5 min. at 70° F. (21° C.) in standard X-ray developer. These conditions will produce enough contrast for most castings.

TABLE I.—*Penetrating Power of X-Rays.*

Power of Set, kV.	Thickness Penetrated, in.		
	Magnesium	Aluminium	Bronze
100	1.25	1.0	0.1
150	2.5	2.0	0.5
250	9.0	7.0	2.0
500	Not recommended	Not recommended	3.5
1000	"	"	6.0

Instead of an X-ray set, it is now possible to make use of certain radioactive isotopes as sources of radiation. Although they are not of great use for light alloys, the advent of radioactive sources has added considerably to the scope of radiography. The main isotopes available that are of interest to the industrial radiologist are given in Table II.

A drawback to the use of isotopes is their gradually decreasing activity, indicated by the half-life figures given in column 3 of the table. This is particularly

important in the case of iridium. Nevertheless, this isotope has been used more extensively than any other for radiographic work, its convenient power and availability having made its use a practical proposition. Cæsium, which is very similar in wave-length of radi-

TABLE II.—*Radioactive Isotopes Used in Radiography.*

Source	Power of Equivalent X-Ray Set, kV.	Half-Life	Thickness Penetrated, in.
Co <sup>60</sup>	1200	5.3 years	1-9 of bronze
Ta <sup>182</sup>	1100	111 days	1-7 "
Cs <sup>137</sup>	700	33 years	$\frac{1}{2}$ -4 "
Ir <sup>192</sup>	500	74 days	$\frac{1}{2}$ -3 $\frac{1}{2}$ "
Tm <sup>170</sup>	84	129 "	Up to 1 of Al

ation emitted and has a longer half-life, would appear to be more useful.

Co<sup>60</sup> is the most powerful isotope commercially available, and its radiation is capable of penetrating thick sections of dense material. At the other end of the scale, thulium would be useful for light alloys were it not for the fact that its very low rate of emission makes the exposures far too long for ordinary work. Its use is therefore confined to cases where the source of radiation must be very small for insertion into a cavity inside the casting. The comparatively short half-life of the isotope detracts from its usefulness, in view of the fact that it will be rarely employed.

The method of taking a radiograph with an isotope is essentially the same as with X-rays. With a given source, the radiation is fixed, and if the source-film distance is kept constant, the only variables, for a given material under examination, are exposure time and section thickness. A chart relating these two factors can easily be prepared, and if an isotope of long half-life is used, little allowance need be made for the diminution in strength of the radiation.

Because of the low contrast that results from the short wave-length of the radiation from isotopes, it is generally possible to use high-contrast films for examining all but the thickest castings.

### 2. FACTORS AFFECTING QUALITY OF RADIOGRAPHS

The two main factors determining the quality of a radiograph are linear resolution and contrast. It will be realized that the sharpness of the X-ray image depends entirely on geometrical conditions, namely (a) the area of the X-ray source, (b) the source-film distance, and (c) the casting-film distance. Clearly, for maximum sharpness (a) and (c) should be as small as possible and (b) as large as possible. For most purposes, where (a) is 4 × 4 mm. and (c) is 15 cm. or less, (b) can be 150 cm. These conditions give adequate sharpness in view of the fact that most films are not capable of recording the greatest degree of resolution obtainable from an X-ray tube. If the finest possible detail is required, high-resolution film must be used.

With a given degree of sharpness, the extent of defects revealed by a radiograph will depend entirely on differences in photographic density. These in turn depend on changes in dimensions or density of the casting under

\* See, for example: J. A. Crowther (editor), "Handbook of Industrial Radiography." 1949: London (Edward Arnold and Co.); A. St. John and H. R. Isenburger, "Industrial Radiography." 1943: New York (John Wiley and Sons, Inc.); London (Chapman and Hall, Ltd.).



examination. Essentially, contrast is determined by the kilovoltage of the X-ray set or the nature of the radioactive isotope being used. The longer the wavelength of the radiation, the greater is the contrast in the radiograph. Contrast may also be controlled to a limited extent by the type of film used and by the development time.

Loss of contrast, and therefore sensitivity, is frequently caused by scattering of the X-rays by the casting. Scattering can lead both to overall reduction of contrast and to local effects which may often be quite severe. There may be no obvious signs of scattering in the film, and hence all possible precautions should be taken against it, for otherwise large defects may be completely obscured.

The best way of reducing general scatter is by the introduction of metal filters either at the X-ray tube or between the casting and the film. With a filter at the tube, soft X-rays, which are principally responsible for scattering, are prevented from reaching the casting; with a filter between the casting and film, scatter itself is reduced. All films must have a substantial backing of lead to prevent back scatter. Thin lead screens are widely used as filters, those commonly employed in the front of the film being 0.004 in. thick, and those at the back 0.006 in. thick. The shape and material of the casting play a large part in the production of scatter, and to reduce it local measures may have to be adopted. For example, heavy pastes can be used to smooth out contours or, in the case of very complicated castings, immersion in a suitable liquid may be helpful.

Because of the much shorter wave-length of the radiation from isotopes in comparison with X-radiation, it is frequently unnecessary to take any precautions against scatter other than the use of lead screens on castings of dense metal. This fact is of considerable practical advantage and may in some cases warrant the use of isotopes for examining castings of thinner section than normal, solely on account of the reduction in scattering.

### 3. RADIOGRAPHIC PROCEDURE

The practical application of the factors described above to a particular casting calls for considerable thought and should be carried out by an experienced radiologist. The problem is not made easier by the need, on grounds of cost, to keep to a minimum the number of films used on any one casting.

The casting must first be studied carefully to try to meet the following conditions:

(1) Each section should be viewed clearly and as far as possible unobscured by other parts of the casting.

(2) Each section should be as close to the film as possible, and the beam should pass normally through the section to be examined. This is to avoid distortion and so make possible a more accurate diagnosis.

(3) The exposure should be correct for the area being dealt with, to achieve the desired density in the final radiograph.

(4) It is extremely useful if each section can be radiographed in two directions.

With castings other than the simplest, it is not possible to fulfil all these conditions. A compromise must be made, and it is in balancing the various requirements that skill is needed.

Quite often films are placed inside castings to cover

sections which are otherwise hidden. It is also frequently necessary to stipulate accurately the angle at which the X-ray beam must strike the casting to examine a particular junction free from other sections. If a casting has appreciable depth, it may be an advantage to take the radiographs with the top and bottom alternately placed on the film.

In materials prone to very fine defects such as micro-shrinkage, the film must be capable of rendering the finest detail. Unfortunately, these films have high contrast and frequently two exposures must be made in the same direction to accommodate the variation of thickness in the specimen. The range of thickness permissible in one radiograph is surprisingly low; with a not very critical technique, the thickness range cannot be more than 3:1.

In the development of a technique for radiographing a casting, it is common practice to determine sensitivity by means of a penetrameter. Sensitivity is usually quoted as a percentage and is the amount of defect shown compared with the thickness in which the defect is present. To find the percentage sensitivity, a step wedge of the same material as the casting is placed on the latter and the thickness of the thinnest step shown is compared with the specimen thickness. In addition, holes are drilled through the steps, and this helps to determine the actual step visible. As the usual percentage required is 2%, for specimens 1 in. thick, a step of 0.020 in. will be shown. It is not difficult to achieve a  $\frac{1}{2}\%$  sensitivity, so that the wedge must have a step as fine as 0.005 in.

Whilst a certain percentage sensitivity is a convenient means of setting a standard, it would be of little use to produce radiographs to this requirement. Most light-alloy radiographs surpass this, but unless the linear resolution is adequate, the radiographs would not be critical enough to reveal the defects which are of most concern.

Thin wires are sometimes used to measure the resolution obtained, but generally it is better to arrive at the sharpness from theoretical considerations, knowing that the geometrical conditions are fundamental.

As many requirements as possible having been satisfied, the exposure time should be set. This is generally taken from previously compiled charts, prepared to suit a density selected to appear in the final radiograph. This density has increased in recent years. At one time 0.7 was considered sufficient, but now a density of 4 is not unusual, 2 being adequate for most casting radiographs, provided that the illumination is sufficient. The explanation that a higher contrast is developed with the greater densities is not altogether convincing, as experiments with a different type of film will prove. A density of 2 will permit a reasonable variation on either side of the value, inevitable with the wide differences in section present in most castings.

Radiographs should be viewed in subdued lighting of sufficient intensity to permit examination of the casting for fairly obvious defects. If possible, the radiograph must be interpreted with the casting itself at hand.

The illumination should be variable, or at least units with different intensities should be available. It should be possible to mask these to avoid dazzle. It is not necessary for the source of light to be as large as the radiograph, since it is possible to study only a small area at one time.



Interpretation can be based only on experience gathered by breaking up and sectioning castings, and by liaison with the foundry. In some instances a particular defect cannot positively be identified. By systematic elimination of faults in the foundry, however, it is possible to establish the cause and thus arrive at a diagnosis.

Defects on radiographs can be classed as local and general. Inclusions can be of material either less or more dense than the main body, though there are generally more voids than inclusions of a heavier nature. Local defects include shrinkage, blowholes, tight blows, turbulence or oxide, cold shuts, misruns, cracks, and dense inclusions. General defects cover gas porosity, micro-shrinkage or porosity, coarse grain, and segregation.

## VIII.—DEFECTS REVEALED BY RADIOGRAPHY

### 1. SHRINKAGE

(Figs. 1-8, Plates LV and LVI)

The series of radiographs in Figs. 1-8 show examples of shrinkage—one of the most difficult of the foundryman's problems. The wide range possible from gross macro-shrinkage to fine micro-shrinkage is clearly illustrated. The unusual formation in Fig. 1, which occurred in magnesium-zirconium alloy D.T.D. 748, is probably due to shrinkage plus a blow and involves also a hot tear. Shrinkage cavities of typical filamentary appearance in aluminium-silicon alloy LM8 are visible in Fig. 2, and may be compared with the smoother, more pipe-like shrinkage exhibited by the unalloyed high-conductivity copper in Fig. 3. Figs 4-6 represent the extremely troublesome general micro-shrinkage found in the aluminium-magnesium alloy L53. The degree present in Fig. 6 is the finest capable of being shown in a print, but even finer degrees are of concern to the radiologist. The strongly directional pattern seen in Fig. 5 is obviously influenced by the section of the casting and the consequent heat gradients.

Typical layer-type shrinkage is present in the magnesium-zirconium alloy casting shown in Fig. 7, which also contains several oxide skins. Fig. 8 indicates how localized this general defect can sometimes be. The area of micro-shrinkage actually occurred at a junction in a casting in magnesium-aluminium alloy L124. The fact that the defect was associated with the change in dimension first resulted in a misleading radiograph, because of the clear demarcation of the shrinkage zone. The radiograph now reproduced was taken from a cut-out piece with its faces machined parallel to obviate the confusion caused by the change in section.

All the shrinkage illustrated, with the exception of Fig. 6, is unusually severe and would have a significant effect upon properties.

In connection with the micro-shrinkage shown in Figs. 4-8, it is evident that, apart from their coarseness, the voids are clearly visible in the radiographs because their main dimension coincides with the axis of the X-ray beam. This particular alignment of the voids occurs frequently in micro-shrinkage, the extent depending on the defective area and the direction or mode of freezing. Obviously the size of these voids is of a very small order, and their detection calls for the highest resolution obtainable. As the pattern of the defect cannot be

forecast, the advisability of radiographing any individual section in more than one direction also becomes apparent. Furthermore, as this particular defect is liable to occur at a junction, there is a danger of its being overlooked because of the wide variations in film density due to the change in thickness of the casting. It may be necessary to reduce the overall contrast of the radiograph to give an adequate rendering of the varying sections. Since it is essential to utilize the degree of resolution obtainable with high-contrast film, the best means to reduce the contrast is by employing high kilovoltages.

It follows that, for alloys liable to contain fine micro-shrinkage, the finest resolution possible should be employed and the highest contrast allowed by the range of densities permissible in the final radiograph or radiographs. This condition applies to all magnesium-base alloys and to the aluminium-magnesium alloy L53. All other defects which one may expect to find by X-rays in aluminium alloys can be detected on medium-contrast film.

### 2. GAS POROSITY IN ALUMINIUM ALLOYS

(Figs. 9-11, Plate LVIII)

Figs. 9-11 are concerned with another common problem encountered in foundry practice—porosity due to gas pick-up on melting or from the mould. Again, very coarse examples are shown, as it is not possible to reproduce in a print the fine gas porosity which causes trouble with alloy L53. Generally it is easy to identify gas porosity by the characteristic globular appearance, but unfortunately in the aluminium-copper alloy D.T.D. 304 and in L53 alloy it assumes the angular formation associated with micro-shrinkage. When it is as coarse as in the aluminium-silicon alloy specimens shown in Figs. 9 and 11, it is fairly safe to attribute the porosity to gas, but with less coarse examples not even a micro-section can afford definite proof. It is interesting to note in Fig. 11 that a shrinkage cavity occurs in the casting exhibiting the lesser degree of porosity. This is a reliable indication that the particular casting was poured subsequently to that showing gas effects only, i.e. the casting temperature was lower. This resulted in a reduction in the volume of gas coming out of solution and a shrinkage cavity formed. Fig. 10 shows the development of fairly coarse porosity in the aluminium-copper alloy D.T.D. 304, such as would probably become visible on fine machining. Gas porosity, unless very severe, does not reduce the mechanical properties appreciably, and the casting will very often stand up to pressure testing. This type of defect can be successfully treated by impregnation.

### 3. OXIDE INCLUSIONS AND BLOWS

(Figs. 12-16, Plate LVIII)

The defects shown in Figs. 12-14 all result from a poorly designed running system and are attributable to turbulence and oxide inclusions. This type of defect manifests itself in a series of badly formed cavities. Figs. 15 and 16 illustrate blows.

The castings in Figs. 12-14 exhibit marked defects, which could be detected by the crudest X-ray techniques. The dense inclusions in Fig. 12 (magnesium-thorium alloy ZT1) are probably due to reaction of the zirconium with the sand. (This figure also shows sealed shrinkage,



discussed later.) In the other examples, turbulence has created voids and oxide has formed round the holes. The importance of oxide inclusions is obvious from the radiographs, especially in the severely affected examples shown. Isolated cavities in castings that are not required to withstand pressure and are situated in areas that do not require machining, are unimportant.

The blow illustrated in Fig. 15, which occurred in magnesium-zirconium alloy D.T.D. 748, is exceptional; nevertheless, when a defect of these dimensions is present, it can easily be overlooked because it may appear to be included in the design of the casting. With most blows, sand is present in the void. This is the case with that shown in Fig. 15, but Fig. 16 would not illustrate the effect, as the blow concerned is due to a chill. This particular blow is covered only by a very thin skin of metal on the chilled face.

The effects of these circular defects are comparatively easy to assess, since they represent a loss of section equal to their size, which involves a simple estimation. Defects of this order are easily detectable, but very fine blows present one of the most difficult problems in radiography. It has not been found possible to reproduce a really "tight" blow from a radiograph. In some cases, even when a blow is connected to the surface, crack testing will not reveal it, because the gap is too narrow to admit the penetrant fluid. This is an additional reason why sections should be examined in two directions, in the hope that the X-ray beam will in one instance traverse the long axis of the defect.

#### 4. CRACKS

(Figs. 17-20, Plate LIX)

Various types of crack are shown in Figs. 17-20. The cracks in Fig. 17 (magnesium-aluminium alloy L122) and Fig. 20 (magnesium-zirconium alloy D.T.D. 748) are of extraordinarily large dimensions and obviously occurred at the solidification stage.

The attempted repair of a magnesium-aluminium casting by welding is illustrated in Fig. 19. This has caused cracking, and the dense inclusions seen in the radiograph are spattered tungsten from the electrode.

Most of the apparent cracks in Fig. 18 are not cracks at all, but marking caused by electrostatic discharge on the film. Some cracks were, however, present. The problem which this figure illustrates was rendered even more difficult because the cracks did not show up on crack testing. The defective castings were eventually sorted out by a further radiography.

The effect of cracks is well known and they cannot be permitted to appear in the finished casting. A crack must be removed and further examination carried out to prove that it has been completely eliminated. It may be necessary to effect a repair to bring the casting back within dimensional tolerances. If so, further X-ray and crack testing must be applied.

#### 5. SEALED SHRINKAGE OR TEARS

(Figs. 21-24, Plate LX)

These radiographs illustrate a rather unusual defect known as sealed shrinkage or tears, where the void or rupture is sealed with the dense constituent. This occurs either in a large thin, even section, or in a par-

ticular area of stress developed as a result of unsatisfactory design of the casting. The effect on the strength is difficult to determine, since if the tear is completely sealed, practically no reduction in properties results. If, however, there has not been complete sealing, the effect is as bad as that of a crack. Often this is difficult to confirm or deny by X-rays, because of the extreme fineness of the gap. Very critical shots should be taken on high-resolution film in several directions. It is also worth while to conduct critical crack tests in the affected area, since in some cases the defect extends to the surface.

#### 6. DENSE INCLUSIONS

(Figs. 25-28, Plate LXI)

All these radiographs show inclusions denser than the parent material. The inclusions in Fig. 25 (magnesium-aluminium alloy L122) can be recognized as flux from the flaky appearance, with indefinite boundaries. Fig. 26 shows zirconium-rich inclusions, uniformly scattered, in magnesium-zirconium alloy D.T.D. 748. The probable cause is pouring too near the end of the pot, but the defect occurs repeatedly in some foundry jobs. In this case, the inclusions are probably due to reaction of zirconium with the sand, which tends to occur where a fairly large quantity of metal flows over long distances.

A local area of dense inclusions in this alloy, almost certainly attributable to sand reaction, is shown in Fig. 27. Very misleading indications are obtained on crack testing, as the defect is not at all serious. In Fig. 28 is illustrated a rather large isolated inclusion in D.T.D. 721 alloy, having its origin in the melting pot.

Dense inclusions in general have little effect on properties unless present to the extent shown in Fig. 26. The type illustrated in Fig. 25, however, with its flux inclusions, cannot be tolerated. In all probability surface corrosion will be evident.

Machining difficulties can be caused by dense inclusions, as they are appreciably harder than the surrounding metal.

#### 7. MISCELLANEOUS

(Figs. 29-32, Plate LXII)

The magnesium-aluminium alloy (L122) casting shown in Fig. 29 contains an extremely fine misrun or cold shut, not detectable by penetrant flaw examination. The apparent defect at the top of the radiograph is the pressure mark of a thumb nail, caused by undue flexing of the film.

Fig. 30 shows segregation and a dense inclusion in magnesium-zirconium alloy D.T.D. 748. The casting was probably poured too near the end of the pot, when the alloy was zirconium-rich, as confirmed by the large flake of dense material.

The difference in grain between two castings in magnesium-aluminium alloy L122, as revealed by X-rays, is illustrated in Fig. 31. The grain-size of the lower casting is so coarse that a diagnosis could be made without further check; in cases where the difference is not so marked, another sample for comparison would be needed.

Fig. 32 is an enlarged radiograph of a test-piece prepared for assessing the degree of resolution of X-ray film. Three 55° angle slots were cut lengthwise in a block of magnesium 0.4 in. thick × 1 in. wide × 2 in.

long, to depths respectively, of 0.002, 0.004, and 0.006 in. and of a corresponding width at the top surface. Determination by eye of the visibility of the slots on the radiograph gave a measure of the sensitivity of the film. The original radiograph was prepared on a normal X-ray, double-coated, high-resolution film, and the finest slot was just visible in a contact print. To allow for losses in reproduction, a  $\times 4$  enlargement has been made. The two coarser lines are easily visible.

## IX.—USING THE RESULTS OBTAINED

In the achievement and the maintenance of quality, a good deal can be learned from the keeping of records. Statistical methods are dealt with elsewhere in the symposium.\*

It behoves the Non-Destructive Testing Department to maintain adequate records so that it may keep the foundry fully informed on points of detail and on general trends. In return it is also necessary for the foundry to inform the Non-Destructive Testing Department of changes in methods so that appropriate notes can be added to records kept. It is advisable with any important job to keep a detailed record of every casting in chronological order of receipt and to cross-reference this with a note of the sequence of pouring.

Although the foundry personnel may call twice a day, or even more frequently to see films of castings, a record should be sent to them. X-ray films should not leave the department, because of possible damage, so that a sketch must be made to indicate any defects present. These reports should show the total number of castings received and the casting or pouring number. The castings are then grouped according to the defects, and some common trend may emerge. Even if a casting is not rejected, a tendency to deterioration should be notified to the foundry immediately so that remedial measures can be taken.

A certain amount of discretion is required on the part of those preparing the reports, since it is impossible to send a note in respect of defects seen in every production casting. The presence of a random fault is not so important as evidence of some departure from good practice in the foundry. It is also necessary to notify the foundry at the sample stage if there are no defects in a casting.

In some cases it is helpful to find the exact position of a defect, and where shots can be taken in two planes, this is quite easy. If this is not possible, a stereo-radiograph can be taken by moving the X-ray tube a definite distance after an exposure and making a second exposure, both images being recorded on the same film. It is then a simple matter to measure the image shift and by geometry to fix the distance of the defect from the surface of the casting. Sometimes the very sharpness or otherwise of an easily recognized defect will enable the experienced radiologist to estimate the distance of a

defect from the surface. When the actual thickness of the defect is required, the simplest procedure is to radiograph the specimen with a block containing an artificial series of defects and measure the film density in both the real defect and the nearest matching artificial defect. A similar method can be used for the accurate measurement of wall thickness at some otherwise inaccessible position in a casting. These tests must always be done by strict comparison to rule out factors such as difference of material, variation in the film speed, and degree of development. There must also be no variation in target-film distance or specimen-film distance.

Even when every precaution and care has been taken it is regrettably true that defects in a casting can remain undetected by any method or combination of methods of examination. The amount of such defects is small, but it can nevertheless be significant. Full coverage can be given only by breaking up castings and concentrating on the areas known to be inadequately examined. Where appropriate, all breaking up should be done after heat-treatment, since the discoloration which then occurs in a number of alloys makes the defects easier to find. Ductility can also be assessed.

The reports from the Non-Destructive Testing Department to the foundry should always be accompanied by a statement on any break-up tests carried out, and it should be the practice that no new casting is approved until such a break-up test has taken place. Break-up checks should be carried out at intervals, depending on the job and the effectiveness of the examination, and it will be seen from a description of the defects and alloys that this will also depend upon the material.

There is every indication that in the future castings will be called upon to perform even more arduous duties. To assist this development, non-destructive testing methods will have to progress, though even at present very few defects escape detection when a casting is subjected to a comprehensive examination. With the reduction of costs which is bound to come, castings previously unexamined for economic reasons will be dealt with.

It is hoped that the main developments will take place in the field of ultrasonic testing, since this method holds the greatest promise of increased speed and reduced cost.

In fluoroscopy the image intensifier—a recent development by which the brightness of the image on the screen can be greatly increased—should make it possible to examine all but the most critical work by screening only.

## ACKNOWLEDGEMENTS

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\* A. R. Martin, *J. Inst. Metals*, 1956–57, **85**, (6), 209.



By A. B. McINTOSH,† Ph.D., B.Sc., F.R.I.C., A.R.C.S.T., F.I.M., MEMBER

## SYNOPSIS

Niobium is of interest for atomic-energy purposes because of its high melting point, excellent compatibility with uranium, good high-temperature strength, and suitable physical and mechanical properties. The metal shows excellent corrosion-resistance to all acids except hydrofluoric, but is rapidly penetrated by caustic alkalis. With pure liquid metals, niobium is satisfactory for service at 600° C. and upwards, but the corrosion rate is markedly increased by small oxygen concentrations. The possible development of alloys possessing high-temperature strength and oxidation-resistance is discussed, and it is concluded that alloys with selected transition metals with interstitial solute additions may be of interest for both purposes.

## I.—INTRODUCTION

FOR use within the fission zone of nuclear reactors which have to work at high temperatures, normal and orthodox engineering materials are unsuitable, either because they absorb too many neutrons or react with the fuel. Because of this, attention has been directed to metals formerly regarded as rare, and great advances have been made in the development of such materials for engineering use.

Among other metals, niobium was selected for investigation, and attention was focused on the economic extraction of the metal from its ores, and on methods of ensuring maximum purity. As a result, niobium has been produced in a more ductile state than ever before, and comprehensive experimental programmes to determine the physical and mechanical characteristics of the pure metal and its alloys, necessarily undertaken to develop the use of the metal for atomic-energy purposes, have disclosed its potentialities in other fields.

## II.—BASIS OF SELECTION AS A CANNING MATERIAL FOR NUCLEAR REACTORS

The method used by the Industrial Group of the United Kingdom Atomic Energy Authority for the selection of materials for reactors has been surveyed by McIntosh and Bagley.<sup>1</sup> Metallic uranium is sheathed or canned to prevent reaction with the coolant and moderator, and, in addition to possessing specific chemical, physical, mechanical, and nuclear properties, the canning material should be easy to fabricate and join.

### 1. CHEMICAL PROPERTIES

A canning material must remain compatible with the fuel and coolant under the most rigorous conditions of reactor operation. Theoretical and experimental considerations led to the conclusion that, together with other metals such as tantalum, molybdenum, and tungsten, niobium was suitable as a container for uranium at the required high temperatures, and that it could be used with safety in liquid sodium or sodium-potassium alloy.

### 2. NUCLEAR PROPERTIES

The neutron absorption cross-section of any canning material must be as low as possible, because of the effect

on neutron economy and consequently on the required degree of enrichment of the fuel. In the handling of radioactive wastes, induced radioactivity resulting from irradiation should be as low as possible. Niobium is, for these reasons, preferable to tantalum, and for use in atomic-energy applications the niobium should have as low a tantalum content as possible. For other engineering applications, this may not be necessary.

### 3. PHYSICAL PROPERTIES

The maximum operating temperature, and consequently the thermal efficiency of a nuclear reactor, are influenced by the melting point of the canning material, which should be as high as possible. Good thermal conductivity is necessary for efficient heat transfer from the fuel to the coolant stream. Any essential alloying needed to obtain enhanced mechanical properties must produce no more than the minimum reduction in thermal conductivity. Preferably, the thermal expansion of the can should be similar to that of the fuel to avoid differential-expansion problems. Finally, especially with gas-cooled reactors, the vapour pressure of the can material at its operating temperature must be sufficiently low to prevent loss of the material to the coolant stream, with possible subsequent deposition in cooler parts of the circuit. Even on the basis of physical properties of material now known to be impure, niobium compared well with other metals in these respects.

### 4. MECHANICAL PROPERTIES

The mechanical properties of a canning material should suit the requirements of the particular reactor under consideration. In some reactors it is necessary for the material to restrain the growth of the fuel in a particular direction, and for this purpose it should have high values for yield and ultimate stress, high modulus of elasticity, and high creep strength, together with sufficient ductility to prevent fracture at the operating temperature and to permit its fabrication into the required can shapes. On the basis of the existing information regarding its compatibility, strength, and other properties, niobium appeared to be a suitable material. The question remained whether fabrication would be difficult if it exhibited the brittle-fracture behaviour found in other body-centred cubic metals. Bechtold<sup>2</sup> has shown that tantalum, even

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though it displays the yield phenomena common to b.c.c. metals, is not subject to brittle fracture in tensile tests at  $-196^{\circ}\text{C}$ . Because of their similarity of lattice spacing, position in the Periodic System, and chemical and other properties, it was inferred that niobium and tantalum would probably show similar brittle-fracture behaviour.

### 5. PROGRAMME OF DEVELOPMENT

On these grounds it was considered that niobium would be an important material for reactor use, and work was initiated within the Industrial Group of the United Kingdom Atomic Energy Authority and with suitable industrial firms to determine the best methods of extracting the pure metal, to investigate the effect of impurities and of alloying, to evaluate the physical and mechanical properties, and to develop methods of fabricating the massive metal into the requisite shapes. The details of some of this work are given in the other papers in the present symposium.

## III.—THE PRODUCTION METALLURGY OF NIOBIUM

The initial difficulty on embarking on a programme of niobium development was to obtain adequate supplies of raw material, owing to the increasing demand for tantalum ores abroad. Niobium was not being produced in Great Britain in 1953, and work was initiated to improve known methods of extraction and to explore alternative and possibly superior means of obtaining the pure metal.

### 1. OCCURRENCE

Tantalum and niobium invariably occur together, the principal mineral source of each being an impure niobite-tantalite of iron and manganese of variable composition. This ore is known as tantalite when rich in tantalum, and niobite or columbite when rich in niobium.

The chief source of niobite is Nigeria, where stocks accumulate as by-products from tin-mining. Production increased from 402 tons in 1941 to 2055 tons in 1944, but fell again to 888 tons in 1949 owing to intensive working of the dumps. Other sources have now been located in Nigeria and the Belgian Congo.<sup>9</sup>

### 2. EXTRACTION DEVELOPMENT

Differences in the properties and the available thermodynamic data of niobium and tantalum compounds were studied and, taking these factors into account, existing processes for the separation of niobium were reviewed. Difficulties in procuring niobium ore in 1953 led to the use of available ferro-niobium for the majority of the extraction processes considered. The details, advantages, and disadvantages of the various methods have been reviewed and the conclusions published elsewhere.<sup>4-6</sup>

## IV.—THE CHEMICAL PROPERTIES OF NIOBIUM

### 1. OXIDATION BEHAVIOUR

At room temperature niobium is resistant to atmospheric corrosion, and samples exposed to the weather in an industrial atmosphere for a period of 15 years have undergone only slight tarnishing.<sup>7</sup> Exposure of niobium

sheet in air at  $200^{\circ}\text{C}$ . indicated that only temper films were formed, with no oxygen penetration or embrittlement of the metal. The resistance to oxidation by carbon dioxide at  $500^{\circ}\text{C}$ . and 8 atmospheres pressure has been determined at the Culheth Laboratories. At this temperature a linear rate law is virtually followed, the loose friable grey scale consisting of the low-temperature modification of  $\text{Nb}_2\text{O}_5$ .

### 2. CORROSION BY ACIDIC AND AQUEOUS MEDIA

Niobium possesses excellent corrosion-resistant properties in most acid and aqueous media, owing probably to the existence of a thin oxide layer which protects the underlying metal from attack and renders it passive under most conditions. Only under conditions where the passivity is destroyed by the breakdown of this oxide film does niobium corrode.

The metal has excellent resistance to the common mineral acids over a wide range of concentration and temperature.<sup>8,9</sup> Table I gives the results of laboratory tests carried out on rolled sheet material of high purity.

TABLE I.—Corrosion-Resistance of Niobium in Mineral Acids at  $20^{\circ}$ – $80^{\circ}\text{C}$ .<sup>8</sup>

Acid	$20^{\circ}\text{C}$ .	$40^{\circ}\text{C}$ .	$60^{\circ}\text{C}$ .	$80^{\circ}\text{C}$ .
Hydrochloric acid:				
Conc. . . .	Excellent	← Good →		Fair
Dil. . . . .	←	Excellent	→	
Nitric acid:				
Conc. . . .	←	Excellent	→	
Dil. . . . .	←	Excellent	→	
Sulphuric acid:				
Conc. . . .	←	Fair	→	Poor
Dil. . . . .	←	Excellent	→	Good

#### KEY

	Penetration, mm./year
Excellent . . . .	<0.01
Good . . . . .	0.01–0.1
Fair . . . . .	0.1–1.0
Poor . . . . .	>1.0
Dilute Acids = 10 vol.-% Concentrated Acids	

In its resistance to acids, niobium resembles tantalum and titanium, and it is practically unattacked in nitric acid at all concentrations and in dilute hydrochloric acid. It has good resistance to concentrated hydrochloric acid below  $60^{\circ}\text{C}$ . and a fairly good resistance below  $80^{\circ}\text{C}$ . (penetration rate 0.24 mm./year at  $80^{\circ}\text{C}$ .). In dilute sulphuric acid it again shows excellent resistance, though it is attacked to some extent by the concentrated acid (penetration rate 1.5 mm./year at  $80^{\circ}\text{C}$ .). However, even in this severely corrosive environment niobium is probably superior to most other metals, except tantalum and platinum.

Solutions containing the fluoride ion rapidly attack niobium, probably with the formation of complex fluoniobate ions.

Although corrosion-resistance in alkalis has not been investigated so thoroughly, the results of Fontana<sup>9</sup> suggest the resistance of niobium to 5% sodium hydroxide at  $100^{\circ}\text{C}$ . (0.5 mm./year penetration) is not good. The metal is probably attacked by caustic alkalis to give solutions containing the niobate ion.

Tests in sodium salts, lactic, acetic, and perchloric acids, 5% phenol, and several acid writing inks have been carried out and no corrosion of niobium whatsoever reported.



## 3. NIOBIUM AND LIQUID METALS

In recent years much interest has been shown in the potentialities of low-melting-point liquid metals for heat transfer. They possess higher heat-transfer coefficients than other fluids and are also suitable for service at high temperatures. These properties make liquid metals attractive for electric power-generation systems, particularly for nuclear-power conversion. The successful exploitation of liquid metals calls for structural materials which are compatible with them under operating conditions. An assessment of the behaviour of various metals under these conditions has been made<sup>1</sup> on the basis of their expected or known solubilities or tendencies to compound formation with the liquid metal. Niobium is satisfactory for service with the following pure liquid metals: lithium, sodium, mercury, tin, bismuth, and lead, and also with sodium-potassium alloy. This results from the almost negligible mutual solubilities of niobium with any of these liquid metals, even at 600° C., and in some cases at higher temperatures.

Because of its current importance for nuclear-power plant, the greatest amount of attention has been paid to the compatibility of niobium with sodium and with sodium-potassium alloy, which is conveniently liquid at room temperature. Results based on static experiments<sup>8</sup> show that corrosion in either pure liquid metal at 600° C. is similar and is less than 0.001 in./year. Similar tests, made at various temperatures between 400° and 600° C. with liquid metal of several oxygen contents, have shown that whereas niobium exhibited excellent resistance to the pure liquid metals, the presence of a small concentration of oxygen in the liquid metal caused a significant increase in the corrosion rate. The behaviour of niobium in flowing sodium or sodium-potassium alloy is largely determined by the oxygen content of the liquid metal, and corrosion may proceed by the formation of a non-adherent scale. This corrosion can, however, be reduced to acceptably low values by ensuring that the oxygen level is kept at a minimum. For this purpose it has been possible to design filters, which depend for their operation on the low solubility of Na<sub>2</sub>O at temperatures just above the melting point of the sodium.

## V.—OTHER PROPERTIES OF NIOBIUM

The properties of niobium are discussed in detail by Tottle,<sup>10</sup> but some general properties are listed in Table II to illustrate the wide field of potential applications for this element.

The melting point of niobium exceeds 2000° C., and the metal retains its strength to moderately high temperatures, the ultimate tensile strength showing little variation between room temperature and 500° C.

The mechanical properties, especially the ductility, are dependent on the gaseous impurity content, and for good ductility the most exacting control must be exercised over the atmospheres in which any thermal treatments are carried out or in which high-temperature tests are made.

Niobium, in the annealed condition, is both soft and ductile and can readily be drawn, stamped, or forged into complicated shapes. Its rate of work-hardening is much lower than that of most other metals. Niobium can be machined with ordinary steel tools and can be welded by

electric spot, seam, butt, and roller processes. Arc welding is difficult, but can be achieved by special techniques.

TABLE II.—Physical and Mechanical Properties of Niobium.

Property	Value	Reference
Atomic number . . . .	41	11
Atomic weight . . . .	92.91	11
Density at 20° C. . . .	8.66 g./c.c.	8
Crystal structure . . . .	Body-centred cubic	11
Lattice constant at 20° C. . . .	3.3004 ± 0.0003 Å.	8, 12
Thermal neutron cross-section (2200 m./sec.) . . . .	1.1 barns/atom ± 0.1	13
Melting point . . . .	2415° ± 15° C.	11
Mean specific heat at 0° C. . . .	0.0647 cal./g.	7
Magnetic mass susceptibility . . . .	+2.28 × 10 <sup>-6</sup> C.G.S. units	7
Emissivity . . . .	0.37 at λ = 6500 Å.	7
Thermal conductivity (0°–100° C.) . . . .	0.13 cal./cm. sec. °C.	8
Coefficient of linear expansion (0°–1000° C.) . . . .	6.89° C. × 10 <sup>-6</sup>	8
Specific resistance at 0° C. . . .	15.22 microhm cm.	8
Work-function . . . .	4.01 V.	11
Positive-ion emission . . . .	5.52 eV.	7
Ultimate tensile strength at 20° C. . . .	17.7 tons/in. <sup>2</sup>	8
Elongation at 20° C. . . .	49%	8
Hardness . . . .	Down to approx. 40 V.P.N.	8

It is a relatively good conductor of heat and electricity, the electrical resistivity being about eight times that of copper; its thermal conductivity (0.13 cal./cm. sec. °C.) lies between that of magnesium (0.38) and zirconium (0.04). The work-function of niobium, 4.01 V.,<sup>11</sup> is the lowest of any of the pure refractory metals with the exception of hafnium.

The property possessed by niobium of forming a stable oxide under the action of an electric current in acid solution is notable. This film offers low resistance when the niobium is made the negative electrode, but extremely high resistance when the polarity is reversed and the niobium is made positive.<sup>11</sup> The oxide film is thin and tenacious and shows interference colours.

## VI.—ALLOYS OF NIOBIUM

## 1. ALLOY SYSTEMS

The properties of niobium most likely to promote its use as a structural material are its resistance to corrosion, high melting point, and high-temperature strength. To make the fullest use of these properties, they may require to be further developed, and other properties such as oxidation-resistance, inferior by comparison, may have to be enhanced by suitable alloying. Unfortunately, because of the short history of the metal, very few of the constitutional diagrams are fully known,<sup>14</sup> and even less information exists on the effects of small alloying additions on the mechanical properties and resistance to corrosion and oxidation.

The known binary phase diagrams for niobium alloys (Fig 1), compiled from various sources, can be supplemented by speculations made on the basis of alloy theory.

Such speculations, referring to undetermined systems of interest, are recorded in Table III.

## 2. MECHANICAL PROPERTIES

In view of the lack of information on the mechanical properties of niobium alloys, some attempt must be made to assess the most profitable systems for study. While the metallurgical factors determining mechanical properties, and especially creep strength, are not fully understood, some factors are considered favourable to high-temperature strength, such as increased recrystallization

higher melting point may favour increased recrystallization temperature. Alloys with elements of low melting point, such as lithium, magnesium, zinc, cadmium, mercury, and tin, are likely to be difficult to prepare and may be unsuitable beyond a restricted solid-solution range.

With solid solutions, the hardening produced is greater, the greater the distortion of the lattice, and for any system the maximum effect would be expected from a saturated solid solution. Other effects such as segregation to grain boundaries may be helpful, particularly at

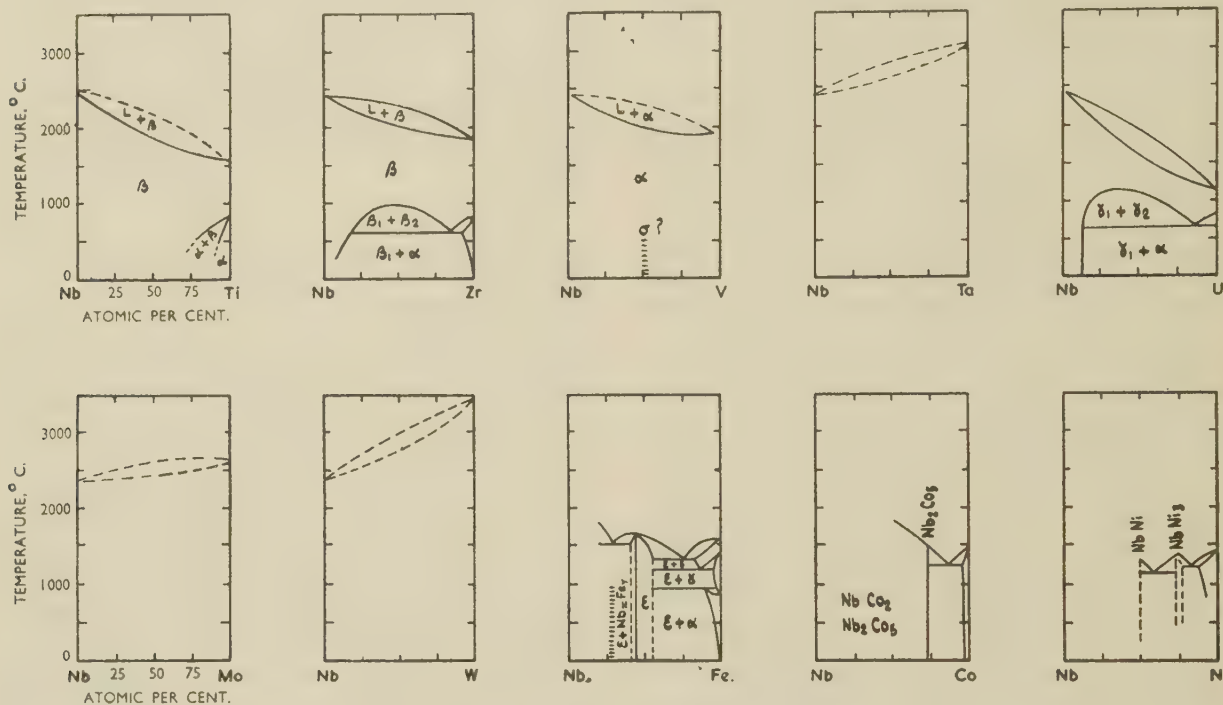


FIG. 1.—Phase Diagrams of Binary Niobium Systems.

temperature, solid-solution hardening, precipitation-hardening, either before or during service, and mechanical hardening by a suitably dispersed stable second phase.

TABLE III.—Niobium Binary Systems for Which no Diagram is Available.

Systems Known to Form Intermetallic Compounds	Systems Likely to Form Intermetallic Compounds	Systems Likely to Exhibit Appreciable Solid Solubility
B	Be	Ag
C	Ru	Al
N	Rh	Au
O	Pd	Cr
Al	Re	Ru
Cr	Os	Rh
Mn	Ir	Pd
	Pt	Hf
		Re
		Os
		Ir
		Pt

A suitable alloying element for conferring good high-temperature mechanical strength will produce one or more of these effects. Elements which result in alloys of

high temperatures where grain-boundary flow may be the important factor in creep. Thus, suitable elements to produce a high value of solid-solution hardening per unit of addition would be those with borderline size-factors, such as iron, chromium, and nickel. If service conditions allow large-scale alloying, titanium, tantalum, and tungsten may be helpful.

In the development of alloys of other metals, solid-solution effects have frequently not in themselves been sufficient to give high creep-resistance, and recourse must be made to strengthening by precipitation-hardening. Because of their tendency to form intermetallic compounds with niobium, the transition elements of borderline size-factor may prove effective in this way. Iron, for example, has been found to produce age-hardening at elevated temperatures. The requirements of such a precipitation-hardening, creep-resistant alloy are complex. Premature over-ageing must be avoided, and general precipitation is preferred to that localized at the grain boundaries. For use over a wide range of temperatures, complex alloys giving hardening effects at different temperatures may be required.

If the rate and nature of the precipitation process may be altered as a result of other factors, such as irradiation,



with possible deleterious effects, an alternative is to rely on the stiffening of the matrix by means of a harder second phase, preferably concentrated at the grain boundaries, an effect which may be found in systems with a peritectoid or eutectoid reaction. The second phase must be stable at the operating temperature, particularly with respect to re-solution and softening. In this respect a compound of high melting point may prove useful, and the transition elements are again of interest because of their tendency to form electron compounds, such as have been found in binary alloys of niobium with iron, cobalt, and nickel. Unfortunately, alloys of niobium with other transition metals may be liable to  $\sigma$ -phase formation, and such phases have been reported<sup>15</sup> in binary alloys of niobium with rhenium, ruthenium, palladium, and platinum. The presence of  $\sigma$ -phase usually causes embrittlement coupled with a decline in strength and oxidation-resistance.

Other substitutional elements likely to form compounds with niobium are the electronegative elements arsenic, antimony, and bismuth in Group VB and tellurium in Group VIB, which are liable to form compounds of the nickel-arsenide type. These compounds will probably be detrimental in niobium alloys because of their low melting points.

The elements likely to form interstitial solutions and compounds should also be considered. Interstitial solid solutions with niobium are probable for hydrogen, oxygen, nitrogen, and carbon,<sup>16</sup> and possibly boron, beryllium, and silicon. All these elements may show solid-solution hardening, ageing, and compound-formation effects; the carbides, borides, nitrides, and silicides of niobium are all hard compounds which are stable up to high melting points. These elements are thus of interest in the development of a creep-resistant alloy. Nitrogen and oxygen have actually been found<sup>8</sup> to have a strengthening effect in niobium, and similar behaviour has been found in tantalum-base alloys.

The effects of alloying on mechanical properties, and especially on creep, are, however, likely to be complex; Glen,<sup>17</sup> for example, in work on steels, has shown that the influence of one alloying element depends on others which are present.

### 3. OXIDATION-RESISTANCE

Niobium shows its group valency in films formed by gaseous oxidation. Examination of oxidation data shows that the best resistance to oxidation is found in metals which form ionic oxide lattices with close packing of both cationic and anionic lattices. Such metals, of which beryllium, aluminium, nickel, and chromium are outstanding examples, have small metal ions, resulting in a minimum oxygen-oxygen distance in the lattice, and a valency of 2 or 3. The cation-cation spacing in the lattice is sufficiently small to give a high activation energy for oxygen diffusion.<sup>18</sup>

Niobium does not show such characteristics, and its oxide has a widely spaced lattice of metal ions at larger interatomic distances than the oxygen ions. Oxides of this type have fairly open structures and show some covalent bonding. They probably grow by an oxygen-ion-diffusion mechanism associated with low activation energy. The activation energy of oxidation of niobium in pure oxygen has been determined as approximately 10 k.cal./g. mole at 500°–800° C.<sup>19</sup>

Much work is required to develop the resistance to oxidation of niobium, and this may be achieved through a study of oxide-film formation on the metal in relation to alloying. Two main approaches may be recommended, although the definition of principles is difficult in view of the linear nature of the scaling in oxidation found by Bridges and Fassell,<sup>19</sup> and confirmed at Culcheth.

Niobium oxide probably grows by oxygen diffusion inwards, so that an alloying solute which diffuses to the surface and preferentially forms a coherent and protective oxide film would prevent the formation of niobium oxide; no evidence, however, is available to aid in the selection of such alloying elements. Extensive sorting tests will be necessary to establish alloys which form oxide films in which the solute atoms predominate.

In an attempt to modify the structure of niobium oxide, alloys of niobium with elements from Groups IVA, VA, and VIA have been selected for study, and alloys of niobium and zirconium have been shown to be promising.

Naturally it should always be demonstrated that improvement in oxidation-resistance does not necessarily entail deterioration in mechanical properties.

## VII.—DISCUSSION

In previous sections the reasons have been discussed for the particular interest of niobium to the United Kingdom Atomic Energy Authority, and the properties which may be of value in other industrial uses have been outlined.

Niobium has no unique physical and mechanical properties, but it enjoys a field of application of its own because it has useful combinations of properties that are not possessed by other metals. For example, niobium resists tearing and splitting more than most other metals when subjected to deep-drawing operations.

The available evidence indicates that niobium is a most attractive corrosion-resistant metal which could be employed for handling the strong mineral acids, with the exception of hydrofluoric acid. The low corrosion rates to be expected under most conditions suggest that the metal could be satisfactorily used in thin sheet form as a corrosion-resistant liner to face reaction vessels and thus increase the plant life of items made of cheaper but less resistant alloys. From the point of view of corrosion-resistance alone, niobium does not in general offer any advantages over tantalum, but the large difference in density between the two metals ( $Nb = 8.57$ ,  $Ta = 16.6$  g./c.c.) would prove a significant point in favour of niobium in circumstances where the weight of the structure is an important consideration. Equality of cost of the metals would result in economy if niobium were used.

There are many applications, for example in chemical-processing equipment and electrical rectifiers and capacitors, where tantalum is now used, for which niobium would be equally suitable, and in which the use of tantalum has resulted mainly from its earlier availability. The two metals are also both suitable for use as gettering materials in electronic tubes as a result of their oxidation behaviour, melting point, high-temperature strength, and low vapour pressure. Niobium is reported to be the more effective in this respect. Although it does not hold

the gaseous impurities up to such a high temperature as does tantalum, less niobium is required than tantalum.

The development of alloys with excellent strength at high temperatures should result from systematic studies of alloying, particularly with iron, cobalt, and nickel, and the interstitial elements, carbon, oxygen, nitrogen, boron, beryllium, and silicon.

Such alloys will be limited in application unless the resistance of niobium to atmospheric corrosion is improved. The approach to this problem may be less systematic, but encouraging results have been shown by the incorporation of alloying elements such as zirconium, which modify the structure of the niobium oxide film formed on the metal. A large field of interesting work arises from a study of the oxidation behaviour of such alloys, with and without the addition of interstitial solutes such as beryllium, boron, or silicon, which may also assist in increasing the coherent and protective nature of the oxide film formed.

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## 1756 THE MELTING POINT OF NIOBIUM\*

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(Communication from the National Physical Laboratory)

#### SYNOPSIS

The melting point of niobium has been redetermined by a technique which avoids the use of refractories. Under approximately full-radiator conditions, the melting point of samples containing about 0.12% gaseous impurities (oxygen and nitrogen) and 1.9% tantalum is  $2468^{\circ} \pm 10^{\circ} \text{C}$ . It is probable that the value for the pure metal is not substantially different.

#### I.—INTRODUCTION

THE present work arose out of a request made by the Ministry of Supply, Division of Atomic Energy,† Risley, Warrington. The material for the experiments consisted of a bar of niobium, 3-4 in. long, and  $\frac{3}{16}$  in. in dia., received from Messrs. Johnson, Matthey and Co., Ltd. A complete analysis of the material was not given, but it was stated that the content of metallic impurities was very low and that the gas content was: oxygen 0.0092, nitrogen 0.0025, hydrogen 0.00013%. Some time after the conclusion of the experiments, it was ascertained both by Messrs. Johnson, Matthey and Co., Ltd., and the

Metallurgy Division, National Physical Laboratory, that the tantalum content was  $1.9 \pm 0.1\%$ .

#### II.—PREVIOUS DETERMINATIONS

The earliest determination of the melting point of niobium appears to be that carried out by von Bolton, who reported a temperature of  $1950^{\circ} \text{C}$ .<sup>1</sup> It is doubtful, however, whether the purity of the material used was sufficiently high to enable a reasonably accurate determination to be made. The value usually accepted for the melting point is  $2415^{\circ} \text{C}$ ., which is given in a brochure issued by the Fansteel Metallurgical Corporation;<sup>2</sup> the

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‡ Now United Kingdom Atomic Energy Authority.



result is quoted as a private communication by S. Dushman. This value was substantially confirmed ( $2410^{\circ}\text{C.}$ ) by Hansen, Kamen, Kessler, and McPherson<sup>3</sup> during an investigation of the constitution of the titanium-niobium system. However, in the same investigation, these workers determined the melting point of titanium and reported a temperature of  $1720^{\circ}\text{C.}$ , which is considerably higher than recent determinations accepted both in the United States and in this country.<sup>4</sup> It is doubtful therefore whether reliance can be placed on the accuracy of their value for the melting point of niobium. Wilhelm, Carlson, and Dickinson,<sup>5</sup> in an investigation of the constitution of the niobium-vanadium system, have reported a value of  $2420^{\circ}\text{C.}$ , thus confirming the results obtained by the previous investigators. No analyses of the samples after any of the above determinations appear to have been carried out, however.

### III.—EXPERIMENTAL METHOD AND RESULTS

The technique used in the present work was essentially the same as that for determining the melting point of

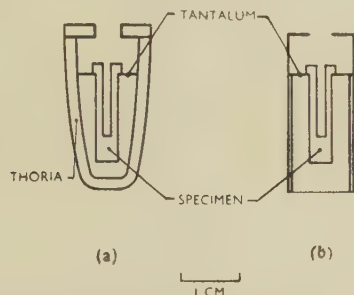


FIG. 1.—Arrangements for Supporting Specimens of Niobium.

titanium.<sup>6</sup> In this method the melting point is taken as the temperature, observed by means of an optical pyrometer, at which liquid begins to form in a deep axial hole in a cylinder of the material slowly heated under approximately full-radiator conditions. Slight modifications of the apparatus were necessary because of the higher temperatures involved. These included a heavier-gauge tungsten-wire heating element and a tungsten rod in place of the sintered alumina tube for supporting the specimen-container. Before the experiments were carried out the pyrometer was calibrated up to  $2500^{\circ}\text{C.}$  in the Physics Division of the Laboratory against a standard tungsten-strip lamp. The accuracy of the instrument was estimated to be  $\pm 20^{\circ}\text{C.}$  in the range  $2000^{\circ}$ – $2500^{\circ}\text{C.}$  At the end of the experiments a careful recalibration of the instrument at  $2468^{\circ}\text{C.}$  (observed melting point of niobium) showed that the accuracy at this temperature was within  $\pm 10^{\circ}\text{C.}$

In the first experiment the specimen rested on the base of a conical sintered thoria crucible fitted with an annular thoria lid. Further experiments with this method were abandoned because contamination of the specimen occurred owing to reduction of the crucible material. Two experiments were then carried out in which the specimen was supported in a tantalum ring so that direct contact between the crucible and specimen was prevented (Fig. 1 (a)). In these experiments melting

occurred at  $2290^{\circ}$  and  $2406^{\circ}\text{C.}$ , respectively. The microstructures of transverse sections of the specimens were similar and showed a light-grey constituent in the grains and boundaries (Fig. 4, Plate LXIII); none of this constituent was observed in the material as received. Vacuum-fusion analyses carried out on the lower halves of each of the two specimens showed that both samples contained appreciable amounts of oxygen and that one had also a high nitrogen content (Table I).

TABLE I.—Hardness, Melting Point, and Gas Content of Niobium.

Specimen No.	Method of Supporting Specimen	D.P.H. No. (5-kg. load, mean of 8-10 impressions)	Melting Point, $^{\circ}\text{C.}$	Gas Content, wt.-%		
				O <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>
As received	...	99	...	...	...	...
2	Tantalum ring in thoria crucible	378	2290	1.34	0.0025	0.00013
3	"	338	2406	0.90	0.05	0.005
4	Tantalum ring and tantalum tube	179	2430	...	...	...
4a	"	154	2472	...	...	...
4b	"	150	2464	0.10	0.01	0.001
5	"	149	2470	0.10	0.01	0.002

It is evident that serious contamination of the specimens had occurred, and in the next series of experiments the vacuum conditions were improved and a tantalum container was substituted for the thoria crucible. The container consisted of two tantalum tubes of different length and slightly different diameter, placed one inside the other. A tantalum ring over the shorter tube supported the specimen, and a similar ring was fitted as a cover over the longer tube (Fig. 1 (b)). The first sample (No. 4) gave a melting point of  $2430^{\circ}\text{C.}$  This temperature was probably low because a main-circuit fuse failed while the reading was being taken and prevented accurate adjustment of the filament temperature. Diamond pyramid hardness measurements made on a flat rubbed on one side of the specimen gave a mean value of 179. After drilling out the melted metal in the core, a redetermination of the melting point gave a temperature of  $2472^{\circ}\text{C.}$  (4a); the hardness determined as before proved to be 154. The melted core was drilled out a second time and the melting point was again determined; a value of  $2464^{\circ}\text{C.}$  was obtained and a mean hardness of 150 (4b). The specimen was porous after these experiments, and the whole was used for analysis of the gas content. The determination of the melting point of a new specimen (5) gave a value of  $2470^{\circ}\text{C.}$  and a mean hardness of 149. No further determinations of the melting point of this specimen were carried out, but the whole was analysed for gas content. In none of the experiments did the specimen weld or stick to the tantalum ring, and consequently it is assumed that no significant contamination of the specimen with tantalum occurred. It was later confirmed that the tantalum content of a specimen after a determination of the melting point was the same as that of the bar as received, namely,  $1.9 \pm 0.1\%$ . The microstructures of the two specimens (4b) and (5) examined in the melted zone were similar and consisted of large equiaxed grains, but no constituent was present in the grains or boundaries (Fig. 5, Plate LXIII). The porosity is associated with the melting.

## IV.—DISCUSSION AND CONCLUSIONS

A consistency in the relationship between melting point, gas content, and hardness of specimens 4-5 is shown, and it may be concluded that the melting point of

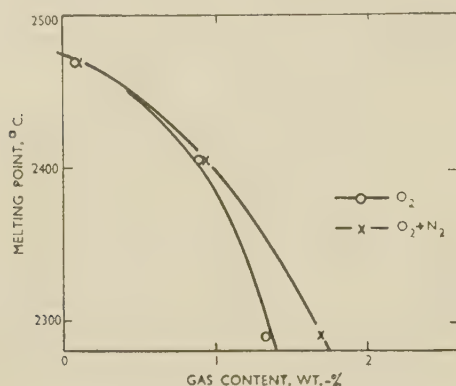


FIG. 2.—Relationship between Melting Point and Gas Content of Niobium.

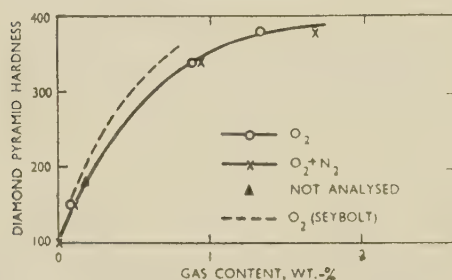


FIG. 3.—Relationship between Hardness and Gas Content of Niobium.

an alloy containing 0.12% oxygen and nitrogen and 1.9% tantalum is  $2468^{\circ} \pm 10^{\circ} \text{C}$ . Extrapolation of the curve in Fig. 2 to zero shows that the melting point of an alloy containing 1.9% tantalum and free from gas is approximately  $10^{\circ} \text{C}$ . higher. According to Bückle,<sup>7</sup> niobium and tantalum form a continuous series of solid solutions, and since the two metals are closely related, it is likely

that these solutions are ideal or nearly so. If this is true, it may be estimated that 2% tantalum will raise the melting point of niobium by approximately  $10^{\circ} \text{C}$ . The melting point of the specimens ( $2468^{\circ} \pm 10^{\circ} \text{C}$ .) is therefore probably not substantially different from that of pure niobium.

The relation between the hardness and gas content (Fig. 3) affords an approximate means of determining the latter, provided that no significant amount of metallic impurities is also present. In an investigation on the solubility of oxygen in niobium, Seybolt<sup>8</sup> has measured the hardness of samples containing up to 0.75 wt.-% oxygen. The oxygen contents do not appear to have been determined by analysis, but were estimated from the amount introduced by gaseous diffusion. Seybolt's results are also plotted in Fig. 3 and, in the range examined, agree approximately with the analytical results of the present work, particularly if allowance is made for small amounts of nitrogen that were likely to be present in the samples.

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# THE PHYSICAL AND MECHANICAL PROPERTIES OF NIOBIUM\*

1757

By C. R. TOTTLE,† M.Met., A.I.M., MEMBER

## SYNOPSIS

The possible employment of niobium or its alloys in reactor components is partially dependent on its possessing suitable physical and mechanical properties. It was therefore necessary to assemble accurate data, covering the range of temperatures involved in reactor operation, on thermal expansion, thermal conductivity, and tensile and creep properties, using metal of a suitable standard of purity for fabrication into complex shapes. Experimental methods already established for metals readily attacked by atmospheric gases were employed.

Thermal conductivity is shown to increase, and tensile properties to decrease relatively slowly, with rise in temperature. Tensile properties are markedly affected by small additions of oxygen and creep measurements are susceptible to serious error if oxygen gains access to the system during long periods of test. Reference is made to preliminary results on the effect of alloying elements.

## I.—INTRODUCTION

### 1. THE PROBLEM

THE design of reactor components calls for accurate data regarding heat transfer and on which to base stress calculations. The complexity of reactor fuel elements in particular involves differential expansion between the fissile material and its container, between the container and sealing arrangements at the ends, and between the container and the support within the reactor core. Variations in the relevant properties with change of temperature must be studied to assess the effects of normal reactor operation and possible fluctuations in power.

Since niobium is known to possess a high solubility for atmospheric gases, it was necessary initially to measure the physical and mechanical properties *in vacuo*, followed by a study of the effects on these properties of a particular reactor environment. The standard of purity of the niobium specimens was determined by the fact that the metal was to be fabricated into complex shapes should it prove suitable for reactor applications. The effect of impurities on the physical and mechanical properties was therefore studied, simultaneously with investigations into the purity attained in production of the metal.

### 2. PREVIOUS WORK

Previous work on the properties of niobium was scanty, and judged to be unreliable because of the impurities present in the metal. Facilities already existed for the measurement of the required parameters on metals reactive to atmospheric gases, and methods for production of high-purity metal were in course of development. Specimens were therefore taken from metal containing some known impurities, together with high-purity material specially prepared for the purpose.

## II.—EXPERIMENTAL WORK

### 1. PROGRAMME

The measurement of thermal expansion and thermal conductivity was the first essential requirement. The existing apparatus in the latter case presented some difficulty, in that large cylindrical specimens were needed, and initially the production of high-purity metal was confined to comparatively small sections. The relationship between thermal conductivity and electrical resistivity could thus be utilized with advantage, since small specimens sufficed for the electrical measurements. Initially, published figures for the Lorentz function were used, but in the later stages of the work, new values became available over a range of temperature. This enabled a preliminary assessment of design data to be carried out before final results were obtained on the thermal conductivity over the complete range of temperature. The resistivity measurements also provided a check on the quality of fabricated metal refined by sintering, since resistivity was found to be proportional to density over the range of porosity encountered after sintering and fabrication.

Tensile properties were measured in order to gain information on stress values suitable for creep tests, and to assist in evaluation of fabrication methods, not only of the metal itself, but also of the final fuel element which might result.

Creep properties were studied only within the range of operating temperatures appropriate to reactors in which the use of niobium might prove an advantage. It was hoped to derive sufficient information to render a reasonable assessment of creep behaviour outside this temperature range feasible, should the necessity arise.

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## 2. MATERIALS

Niobium manufactured in small quantities both in the U.S.A. and the U.K. was available at the beginning of the work. The metal was most readily obtained as sheet, and although the oxygen content was higher than was thought desirable ( $> 0.10\%$ ), the metal could be fabricated with some difficulty. Bar material was often found to be porous or heterogeneous with respect to grain-size and inclusions. In many cases, purchased metal was first worked by rolling, forging, or swaging (where necessary) and then annealed *in vacuo* at  $2200^{\circ}\text{C}$ . for such a time as was found necessary to reduce the oxygen content to less than  $0.05\%$ . When massive specimens were employed, as in thermal-conductivity measurements, it was frequently not possible to work the material, but vacuum-annealing was carried out to reduce the oxygen value.

At a later stage, powder of much lower impurity content became available. Batches of this were cold pressed, sintered at  $2200^{\circ}\text{C}$ ., hydrogen-treated, crushed, degassed, re-pressed, and re-sintered at  $2200^{\circ}\text{C}$ . before working and machining to shape. On occasion, various methods of sintering were under investigation, and specimens were frequently prepared in order to check their metallurgical properties against existing samples.

In general, the niobium used was of  $99.95\%$  purity, and check analyses carried out after measurement of the various properties showed little pick-up of atmospheric gas, purity being usually not less than  $99.90\%$  even after 1000-hr. creep tests. Any serious pick-up could be detected during test by unexpected changes in the creep curve, and if analysis confirmed the suspicions, the results were rejected and the experiment repeated.

Alloys were prepared by two methods. Investigations into the effects of oxygen were carried out by first preparing extremely pure metal, by long periods of vacuum-annealing and re-working, and then soaking the specimens in the gas atmosphere at  $600^{\circ}\text{C}$ ., followed by heating at  $1400^{\circ}\text{C}$ . to homogenize the alloy.

The alloying elements investigated were chiefly those which form simple solid solutions, e.g. metals of Groups IVA, VA, and VIA of the Periodic Table. (Since the influence of irradiation on more complex alloys is not known with certainty, solid solutions were studied for the possible increase in creep-resistance which might result.) Using the principles outlined in a previous paper on alloys developed for creep-resistance,<sup>1</sup> the alloying elements and their concentration were so chosen as to preserve reasonable thermal conductivity and produce some solid-solution hardening. The melting points of those elements which give rise to solid solutions (from the groups referred to above) are high, so that arc melting was employed in manufacture. Mixed powders of the two elements were cold pressed before melting in an argon atmosphere, the furnace having been twice evacuated to a pressure of less than  $10^{-4}$  mm. Hg and flushed with argon before melting began. A small piece of niobium was employed to "getter" the purified argon atmosphere in the furnace, using a separate hearth as a final precaution. Cold-pressed and sintered compacts of the alloys have also been prepared, employing the same techniques as for pure niobium. Both sintered compacts and arc-melted material were swaged and rolled before machining to shape.

## 3. EXPERIMENTAL METHODS

The thermal-expansion measurements were carried out in a modified Gale dilatometer operating in a chamber evacuated to less than  $10^{-4}$  mm. Hg pressure. Precautions to ensure accuracy included a vibrating device to prevent sticking of the clock gauge.

Thermal conductivity and electrical resistivity were measured in an apparatus developed from that described by Armstrong and Dauphinée,<sup>2</sup> using longitudinal heat flow through a cylindrical specimen.

Standard testing machines were employed for studying the mechanical properties, with the incorporation of gas chambers to enclose the specimen, as described by Fenner and Willoughby.<sup>3</sup> In tests carried out at elevated temperatures, a standard heating time of 1 hr., followed by 1 hr. at the test temperature, was adopted, before applying load.

## 4. RESULTS

Values for the thermal expansion of pure niobium are shown in Table I, with a derived equation covering the range of temperature investigated.

Table II gives results obtained on high-density, pure niobium for the thermal conductivity and electrical resistivity.

The tensile properties of pure niobium up to  $550^{\circ}\text{C}$ . are included in Table III. The figures obtained at  $500^{\circ}$

TABLE I.—Thermal Expansion of Niobium.

Temperature, $^{\circ}\text{C}$ .	300	400	500	600	700	800	900	1000
A, $^{\circ}\text{C}^{-1} \times 10^{-6}$	7.31	7.39	7.47	7.56	7.64	7.72	7.80	7.88
B, $^{\circ}\text{C}^{-1} \times 10^{-6}$	7.38	7.54	7.61	7.87	8.03	8.20	8.37	8.52

A = Linear coefficient between  $18^{\circ}\text{C}$ . and stated temperature.  
B = Instantaneous linear coefficient.  
 $L = L_0[1 \times 6.892 \times 10^{-6}t + 8.17 \times 10^{-10}t^2]$ .

TABLE II.—Thermal Conductivity and Electrical Resistivity of Niobium.

Temperature, $^{\circ}\text{C}$ .	0	100	200	300	400	500	600
Thermal conductivity, cal. cm. <sup>-1</sup> sec. <sup>-1</sup> $^{\circ}\text{C}^{-1}$	0.125	0.130	0.135	0.140	0.145	0.151	0.156
Electrical resistivity, microhm. cm.	15.22	19.18	23.13	27.09	31.04	35.00	38.96

TABLE III.—Tensile Properties of Niobium.

Test Temperature, $^{\circ}\text{C}$ .	Limit of Proportionality, tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	Elongation, % on $4\sqrt{a}$	Young's Modulus, lb./in. <sup>2</sup> $\times 10^{-6}$
20	10.8	17.6	49	12.4
200	6.5	15.0	48	10.9
300	6.3	15.5	38	8.0
400	6.5	14.8	28	7.5
500	6.8	15.9	35	6.4
550	4.7	14.4	24	4.7

C. are rather higher than would be expected from the general trend at lower temperatures. The values quoted are the mean of three or four tests.

Creep results obtained to date, on pure niobium and one alloy, are illustrated by Table IV, compiled from



TABLE IV.—Results of Creep Tests on Niobium and Niobium-6½% Molybdenum Alloy.

Material		Temp., °C.	Stress, tons/in. <sup>2</sup>	Time Required for Specified Percentage of Creep Strain, hr.						Minimum Creep Rate, in./in./hr. × 10 <sup>4</sup>	Duration of Test, hr.	Total Creep Strain, %	Oxygen Content, %	
				0.05	0.1	0.2	0.3	0.5	1.0				Before Test	After Test
Pure Niobium														
Swaged bar		600	4	50	160	860	2130	...	...	...	5519	0.306	0.04	0.021
Pressed and annealed slab		600	5	5	15	35	...	165	980	2.3	1359	1.08	0.015	<0.1
As rolled		600	6	40	130	345	1160	...	...	...	...	...	0.04	0.19
Swaged bar		700	1	40	290	1560	...	...	...	...	2314	0.22	0.04	0.22
Swaged bar		700	2	80	205	550	1495	...	...	...	5008	0.36	0.04	<0.1
Swaged bar		700	3	120	220	540	1115	...	...	...	3335	0.40	0.04	<0.1
As rolled		500	10	...	10	18	35	400	1295 (0.6%)	...	In progress	...	...	...
Niobium-6½% Molybdenum Alloy														
As rolled	Rod	600	4	5	20	...	...	...	...	...	600	0.22	...	...
	Strip	600	4	4	45	...	...	...	...	...	550	0.27	0.09	...
As rolled	Strip	600	6	1	2	6	14	50	...	...	500	0.56	0.04	...

graphical records. Tests which were in any way suspect, either on account of impurities in the specimens or of pick-up during test, have not been recorded here. Nevertheless, very few cases of severe pick-up occurred. Oxygen contents in excess of 0.2%, and, in addition, a nitrogen content greater than 0.05%, were regarded as severe pick-up.

Table V shows the effect of oxygen on mechanical properties at room temperature, together with values for the electrical resistivity of the alloys.

TABLE V.—Effect of Oxygen on Electrical Resistivity and Tensile Properties of Niobium at Room Temperature.

Oxygen Content, wt.-%	Electrical Resistivity, microhm cm.	Mean Vickers Hardness No.	Limit of Proportionality, tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	Elongation,* %
0.03	16.25	87	12.6	18.35	29.3
0.161	18.79	194	27.3	34.1	16.9
0.208	22.11	208	30.9	40.7	17.66
0.279	24.12	248	34.6	44.3	20.7
0.315	25.67	278	43.6	60.9	20.5
0.371	26.18	314	47.4	61.0	10.4
0.410	26.59	331	48.1	58.6	9.8
0.565	30.60	390	Specimen cracked before testing		

\* The irregular elongations are due to some specimens breaking in the grips.

It was believed that the alloys on which results were obtained in the first exploration were not representative of the best material that could be prepared, and later work confirms this view. The results quoted in Table VI refer to alloys made from powders of somewhat high impurity content, but indicate the effect of alloying elements on mechanical properties and electrical resistivity. Creep tests on alloys are still proceeding,

and Table IV includes results on specimens of one niobium-molybdenum alloy.

TABLE VI.—Effect of Alloying Elements on Mechanical Properties and Resistivity of Niobium at Room Temperature.

Alloy	U.T.S., tons/in. <sup>2</sup>	L.P., tons/in. <sup>2</sup>	Elong., %	Resistivity, microhm cm.	V.P.N.
5% Mo *	30	24.2	7.7	18.09	131
5% Mo	26.4	21.8	12.3	16.97	150
5% Mo	27	24.3	16.8	...	147
6½% Mo	37.6	...	15.0	...	150
7½% Mo	40.2	30.9	13.32	...	159
10% Mo	31.0	24.2	8.5	17.6	167
5% W	26.0	21.7	11.7	17.2	145
5% W	19.9	13.3	8.9	...	111
7½% W	33.7	25.4	10.4	...	113
10% W	29.7	25.8	9.9	21.1	191
1% Zr	18.8	10.7	18.2	15.82	75
2% Zr	20.0	14.1	11.5	17.53	94
Higher alloys difficult to fabricate, owing to impurity content of zirconium					
10% Ta	26.75	19.7	10.7	...	111
10% Ta	28.7	20.8	19.8	...	74
2% V	24.9	18.9	11.2	...	123
Higher alloys difficult to fabricate, using vanadium of comparatively high impurity content					
2% Ti	18.0	14.1	14.6	18.861	100
5% Ti	24.7	21.7	15.3	...	147
1% Pt	19.4	14.05	13.2	...	94
Niobium †	18.35	12.6	29.3	16.25	87

\* Oxygen content >0.05%.

† As used in preparation of above alloys.

## III.—DISCUSSION

The observed values of thermal expansion show no unexpected trends. The intentional addition of impurities was found to influence the results obtained, and low-density samples used in the initial exploratory work were rejected in view of the effect on thermal expansion. The selection of niobium for reactor applications was not influenced by the expansion data, but the necessity for careful consideration of differential expansion between other metals and niobium became increasingly apparent, particularly in view of the high coefficient of expansion of uranium.

The thermal conductivity of niobium was expected to be inferior to that of its neighbouring elements in the Periodic Table. Molybdenum, in particular, has excellent heat-transfer properties at room temperature. However, the preparation of high-density, pure niobium proved that the thermal conductivity was not so low as had been presumed. The increase in conductivity with rise in temperature is considerable, as Table II indicates, so that at reactor-operating temperatures, the heat-transfer properties are in fact almost equal to those of molybdenum, since the conductivity of the latter decreases quite rapidly with rise in temperature. Reasonable heat-transfer properties imply less-steep temperature gradients through a metal used as a container for reactor fuel elements, and therefore reduced thermal stresses.

The theoretical Lorentz function for niobium is actually lower than the figure obtained from the data in Table II. This is believed to be due, at least in part, to the effect of lattice conductivity, which is not accounted for in the derivation of theoretical values for this function. It was observed that low-density specimens showed inferior thermal conductivity but approached more closely the theoretical value of the Lorentz function at high temperatures.

The tensile properties of niobium show a relatively slow decrease in strength with rise in temperature, but the fall in Young's modulus is rather more marked. The values for limit of proportionality (Table III) indicate an expectation of reasonable creep strength at temperatures up to 500° C., but the high elongation at fracture shows that the ductility of the pure metal is retained. Creep properties were therefore expected to show high initial elongation, but retention of reasonable strength as the temperature increased.

Creep tests (Table IV) are so far few in number, owing in part to rejection of results where some solution of oxygen was suspected, and in part to certain specimens being considered unrepresentative with respect to density, purity, or uniformity of mechanical working. Nevertheless, the results show that niobium does undergo rapid deformation in the primary stage, followed by long periods at low rates of deformation. By comparison with more conventional metals, such as commercial-quality nickel, the creep strength is low until temperatures of the order of 600° C. are reached, when rise in temperature has much less effect on niobium than on nickel. The creep strength at 600° C. was lower than had been expected, so that the effect of alloying on this property took on additional importance in considering possible applications in reactors.

The measurements made on niobium containing

oxygen, in earlier work, revealed that niobium-oxygen alloys were considerably harder than the pure metal, and that any unintentional leakage of air into the gas chamber used in the mechanical tests decreased the rate of deformation remarkably. (This was also observed by Allen and Carrington.<sup>4</sup>) Table V shows the effect of oxygen at room temperature and indicates that reasonable thermal conductivity, accompanied by ductility, should be maintained up to an oxygen content of 0.3%. Work on these alloys was not pursued further in view of the ease with which the oxygen can be removed by uranium in contact with the alloy. In applications where oxygen would remain in solution in the metal, the enhanced creep strength is likely to be of great value.

The effect of alloying elements chosen for their solid-solution hardening of niobium follows the expected trends. The necessity for the use of pure alloying elements, in addition to pure niobium, became obvious during the course of preparation of the specimens. Traces of oxygen or nitrogen gave rise to difficulties either in fabrication or in testing. Vanadium and zirconium proved particularly difficult in this respect. The most consistent results (Table VI) were obtained with niobium-molybdenum alloys. The balance between hardening and ease of fabrication led to the adoption of an alloy with 6% molybdenum as a suitable material for more intensive investigation. Fabrication of thin-walled tubes in this material is still proving difficult, and creep results shown in Table IV are inferior to those on the pure metal. Chemical analysis, including determination of gas content, has failed to account for these differences on grounds of impurity content. No explanation of the hardening produced by molybdenum at room temperature, and the greater deformation in a creep test at 600° C., has yet been found. It certainly appears that oxygen is a far more potent alloying element than many metals which enter into solid solution in niobium.

The effect of alloying elements must take priority in the continued investigation of niobium, particularly in creep tests. Closely allied with this will be the existence of impurities such as oxygen and nitrogen, and their influence on other alloying additions. Development of an alloy with greater creep-resistance than niobium will most certainly necessitate checking of thermal conductivity before application in a reactor can be considered, but thermal expansion is hardly likely to suffer any significant modification.

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## SYNOPSIS

The purification of niobium by sintering *in vacuo* has been studied on both a laboratory and a commercial scale. Gaseous impurities were eliminated by vacuum treatment at temperatures up to 2300° C. When both elements were present, simultaneous removal of oxygen and carbon as carbon monoxide was achieved. In the presence of oxygen, silicon was also eliminated as silicon monoxide.

Ductile massive niobium, containing oxygen 0.05, nitrogen 0.01, and carbon and silicon <0.01 wt.-%, has been prepared on a commercial scale.

## I.—Laboratory Investigation of Purification by Sintering

## I.—INTRODUCTION

A THEORETICAL survey of the requirements that must be met by canning materials intended for use in atomic reactors has been published by McIntosh and Bagley,<sup>1</sup> together with a description of the experimental programme based on the findings of this survey. Among other metals, niobium was selected for possible use in reactors cooled by sodium/potassium, special emphasis being placed on the development of strong, easily fabricated alloys. Attention was accordingly focused on the economic extraction of niobium and on the factors, especially ductility, influencing its fabrication.

After an investigation of the advantages and disadvantages of various extraction processes,<sup>2</sup> it was decided that development efforts should be concentrated on two approaches: (1) the preparation of a pure intermediate double fluoride ( $K_2NbF_7$ ), which can be reduced to metal powder by sodium, and (2) the production of a pure chloride intermediate ( $NbCl_3$ ), which can be reduced by hydrogen or, possibly, by magnesium. The former relies on wet chemical methods for the isolation of potassium niobium fluoride, the separation of contaminants being effected by variations in solubility. Purification by the chloride process depends on selective vapour-phase reductions and on distillation of the volatile chlorides.<sup>3</sup>

The melting point of niobium is in the region of 2460° C.; for sintering, temperatures in excess of 2000° C. are required. Owing to the reactivity of the metal, both melting and sintering must be performed in a chemically inert atmosphere. Even under a reduced argon pressure, the massive metal obtained by either method of consolidation cannot be satisfactorily worked on account of retained gaseous impurities, notably oxygen and carbon, which adversely affect ductility. The work now described indicates how a further purification of niobium may be achieved by high-temperature sintering *in vacuo*.

## II.—IMPURITIES

Although the particular method of production determines the level of impurities, niobium powder may contain up to 0.3 wt.-% hydrogen, 0.5 wt.-% oxygen, 0.1 wt.-% nitrogen, and 0.3 wt.-% carbon.

## 1. HYDROGEN

Niobium takes up large quantities of hydrogen in solid solution. A distended niobium lattice has been observed by X-ray methods<sup>4</sup> in the range 0.0–0.8 wt.-% hydrogen. At higher hydrogen concentrations, the formation of a niobium hydride was indicated by the appearance of a second phase. The removal of hydrogen from niobium has been shown to occur readily at 700° C. *in vacuo* (0.1  $\mu$ ) when the hydride phase is eliminated and the distended body-centred niobium lattice is reduced to normal dimensions.

## 2. OXYGEN

There are three oxides of niobium, NbO, NbO<sub>2</sub>, and Nb<sub>2</sub>O<sub>5</sub>, each existing over a small homogeneous range. Seybolt,<sup>5</sup> using X-ray methods, investigated the solubility of oxygen in niobium in the range 775°–1100° C. and showed that it was temperature-dependent, increasing from ~0.25 to ~1.0 wt.-% in that range.

By extrapolation from lower-temperature data, the standard free energy of formation of the oxides of niobium at 2000° C. is estimated to be –90, –100, and –140 k.cal./g.-mol. oxygen for Nb<sub>2</sub>O<sub>5</sub>, NbO<sub>2</sub>, and NbO respectively. Thus, if oxygen is present as the monoxide or in solution, the equilibrium oxygen pressure is calculated to be equal to or less than 10<sup>–12</sup> cm.

## 3. NITROGEN

Little information on the niobium–nitrogen system is available. Two compounds are reported,<sup>6</sup> Nb<sub>2</sub>N and

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NbN. Ang and Wert,<sup>7</sup> using internal-friction methods, investigated the solubility of nitrogen in niobium over the range 300°–1200° C. and showed that it increased from approximately 0.005 to 0.05 wt.-% in that range.

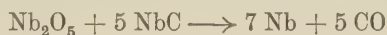
From an extrapolated value of –30 k.cal./g.-mol. of nitrogen for the free energy of formation of NbN at 2000° C., the equilibrium nitrogen pressure is estimated to be  $10^{-2}$  cm.

#### 4. CARBON

Niobium forms one well-defined carbide, NbC, though the existence of lower carbides has been suggested.<sup>8</sup> No precise information is available on the solubility of carbon in niobium, but assuming an interstitial mechanism for solution in niobium, carbon should have a much lower solubility than either nitrogen or oxygen, by virtue of its larger atomic radius. A low solubility would be expected by analogy with tantalum.

#### 5. CARBON AND OXYGEN

A method for the preparation of niobium has been reported<sup>9</sup> in which the carbide and oxide are intimately mixed and held at 1600° C. *in vacuo*. The carbon and oxygen are eliminated as CO in a reaction which may be represented as:



This indicates a possible method of purification from carbon and oxygen where they co-exist in niobium metal, the mechanism being the independent diffusion at high temperatures of the carbon and oxygen to a free surface at which they combine to form a gaseous product. Without data for the activity of carbon and oxygen in solid solution in niobium, it is not possible to estimate the extent of purification obtainable.

The rate-controlling mechanism for this reaction is not likely to depend on the rates of diffusion of oxygen or carbon, since these appear to be high.<sup>10</sup> It is possible, however, that, in view of its low solubility in niobium, the rate of solution of carbon may be the controlling factor.

### III.—PURIFICATION BY SINTERING

The removal of gaseous impurities by a sintering operation probably involves: (a) the solution of the impurity; (b) its diffusion to free surfaces; (c) the formation of elemental gas molecules; or (d) the formation of a volatile compound.

Consideration of the mechanisms suggested above, in conjunction with the data previously given for the gaseous impurities, indicates that:

(i) The removal of hydrogen as gas by a simple high-temperature treatment *in vacuo* should be most readily achieved.

(ii) The removal, by similar mechanisms, of nitrogen should also be possible under high vacuum at higher temperatures, probably in the region of 2000° C.

(iii) The stability of oxygen in niobium precludes any straightforward removal of oxygen in elemental form in practical temperature and pressure ranges.

(iv) The removal of oxygen may be achieved by its

elimination as the volatile oxide of a reducing agent or by the formation of a volatile oxide of niobium.

These considerations led to the investigation of high-temperature sintering of niobium *in vacuo*.

### IV.—EXPERIMENTAL

#### 1. PREPARATION OF COMPACTS

The powders from the various extraction processes were shown by electron-microscope examination to consist of aggregated particles less than 4  $\mu$  in dia., the finest measuring 0.01  $\mu$ . Packing (tap) densities were in the range 1.8–2.5 g./c.c., and strong cold compacts of density 4.0–5.0 g./c.c. were obtained by cold pressing at 10 tons/in.<sup>2</sup> or above.

#### 2. SINTERING PROCEDURE

##### (a) Apparatus

Induction or direct-resistance heating was normally used to attain sintering temperatures of over 2000° C.

For induction sintering a specimen of up to 1.5 cm. in dia. was placed in a transparent silica tube of 3.2 cm. bore, 50 cm. long, and heated by direct susception. One end of the tube was sealed by a rubber ring, with a glass observation window. Shields were used to protect the seal and the window from radiant heat and deposits of volatilized material. The specimen was supported on a rack made from molybdenum or tungsten strips or wires, since preliminary experiments had shown that niobium reacts with alumina, magnesia, or stabilized zirconia, but that line or point contact with molybdenum or tungsten was satisfactory provided that the supports were of small axial cross-section to minimize induction-heating effects.

The tube was evacuated by continuous pumping to below  $10^{-5}$  cm. pressure, although during runs pressures of up to 1 mm. were temporarily recorded when compacts were being outgassed.

The water-cooled power coil of the H.F. generator surrounded the silica tube, and additional cooling was obtained by compressed-air jets. Temperature readings were made with an optical pyrometer calibrated to black-body conditions, applying emissivity corrections determined in early experiments by comparison observations of a deep hole drilled in the compact with the apparent temperature of the exposed niobium surface.

The direct-resistance sintering furnace consisted of a 12-in.-dia. water-cooled, evacuated steel bell, on an insulated steel base-plate through which the electrical and vacuum connections were made (Fig. 1). The specimen, a bar 12 cm. long, was gripped between tungsten pads on water-cooled copper electrodes, the top electrode being adjustable. Direct current of up to 1000 amp. was applied to the lower electrode, which also incorporated flexible water-cooled bellows, the complete arrangement thus permitting movement to take up the shrinkage of about 1.5 cm. which occurred during sintering.

A third method of heating by bombardment with electrons from a heated tungsten filament was used in isolated instances. In these experiments small buttons of niobium, retained on a water-cooled copper hearth,



were raised to temperatures above the melting point. The system was evacuated by continuous pumping to pressures of  $10^{-5}$  cm. or less.

The advantage of this method lay in the higher temperatures attainable, a feature not possible with

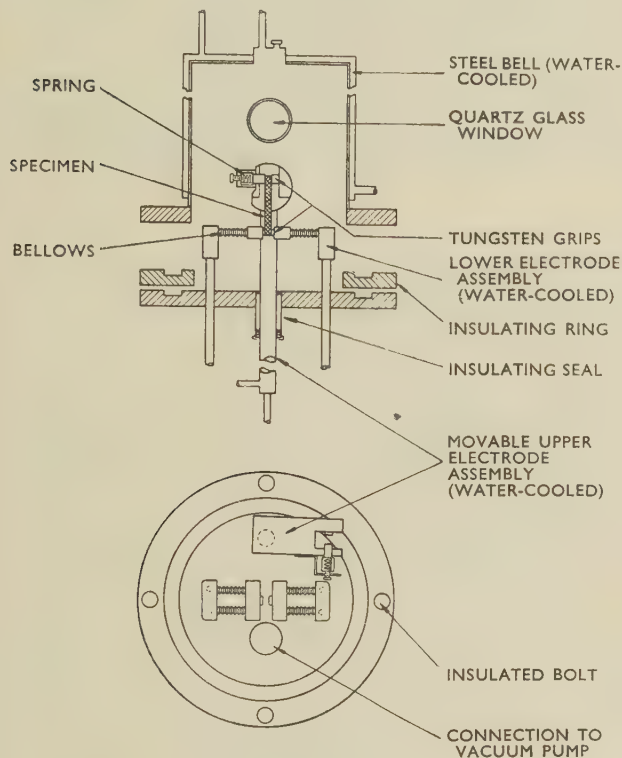


FIG. 1.—Apparatus for Direct-Resistance Sintering.

sintering methods, nor feasible with crucible melting owing to the reaction of the metal with the crucible material.

#### (b) Technique

Outgassing—principally the evolution of hydrogen—at temperatures below  $1000^{\circ}\text{C}$ . tended to break up or crack the compact. Thus a preliminary degassing treatment while the metal was in loose powder form proved desirable.

Rapid evolution of gaseous impurities at high temperature during induction sintering caused local pressure increases in the neighbourhood of the power coil, leading to a sudden and violent glow discharge which, in one instance, melted the compact, molybdenum support and shield, and silica tube within 10 sec.

In laboratory experiments the simplest method of overcoming this effect was by careful control of the power input during the period of high outgassing, to prevent gas concentrations exceeding the level at which ionization, and hence glow, takes place. Sporadic high outgassing rates were, however, frequently encountered, and the development of glow in these instances was prevented by temporary reduction in the field strength.

The ionization of evolved gases in the field of the power coil can also be eliminated by using an indirect heating technique in which the environment of the specimen is electrically shielded by a cylindrical susceptor which heats the specimen by radiation.

High-temperature outgassing in the body of the compact caused swelling and blistering, and necessitated recrushing and resintering.

The rates of heating, and the sintering time and temperature were varied between wide limits. Temperatures in the range  $1700^{\circ}$ – $2300^{\circ}\text{C}$ ., and times of  $\frac{1}{4}$ –24 hr. were used.

## V.—RESULTS

### 1. PURIFICATION

#### (a) Hydrogen

The hydrogen content of powder produced by the  $\text{K}_2\text{NbF}_7$  method averaged about 0.27 wt.-%. That of powder produced by the hydrogen-reduction method was variable, but considerably greater.

Hydrogen evolution began in the early stages of sintering at temperatures below red heat, and rapidly reached a negligible rate at  $800^{\circ}$ – $1000^{\circ}\text{C}$ . Final analysis of sintered ductile metal gave a hydrogen content of <0.001 wt.-% in all material produced.

Hydrogen was readily taken up by niobium at  $600^{\circ}\text{C}$ . to a total approaching 0.8 wt.-%, and resulted in an embrittled metal which could be disintegrated into brittle flakes. Hydrogenation was thus used to assist in recrushing where this was necessary for the completion of oxygen removal.

#### (b) Nitrogen

The nitrogen content of raw powders normally approached 0.1 wt.-%. Analysis of ductile metal after vacuum sintering at  $>2000^{\circ}\text{C}$ . indicated rapid removal of this element. The nitrogen content of small compacts was reduced to  $\sim 0.02$  wt.-% in approximately 15 min. The elimination of nitrogen, having thus been proved, was not studied in further detail, and was consistently achieved to  $\geq 0.01$  wt.-% under the conditions required (up to 8 hr. at  $2250^{\circ}\text{C}$ .) for oxygen purification in the larger compacts.

#### (c) Oxygen

The oxygen content of early powder samples was frequently greater than 0.9 wt.-%, but with development of the extraction processes this was reduced to 0.3–0.5 wt.-%.

Black deposits formed on the cool walls of the silica tube when the sintering temperature approached  $2000^{\circ}\text{C}$ . A simultaneous reduction in oxygen content of the metal was recorded. The fact that no evidence of high-temperature elemental gas evolution was obtained during the sintering of niobium of low carbon content suggested that oxygen was removed in the form of a volatile oxide.

The weight losses recorded during the sintering of oxidized niobium powder or compacts to which  $\text{Nb}_2\text{O}_5$  powder had been added, could not be interpreted in terms of evolution of oxygen gas. Calculations indicated that oxygen and niobium were lost in approximately equiatomic proportions, and X-ray examination of the volatilized deposits removed from the walls of the sintering units confirmed the presence of low oxides of niobium. It is probable that some oxidation of the samples occurred during collection for X-ray analysis.

Chemical analysis of ductile niobium produced by

single-stage sintering of small compacts at 2250°–2300° C. for  $\frac{1}{2}$ –4 hr. showed a reduction of oxygen from an initial level of up to 0.7 wt.-% to a final level below 0.02 wt.-%.

Samples of niobium containing 0.05 wt.-% oxygen were further purified by repeated treatments in the electron-bombardment furnace. After 5 melts the oxygen content was reduced to below 10 p.p.m. Other impurities were reduced to the following levels: nitrogen 40, hydrogen 2, and carbon 20 p.p.m.

The complex behaviour of niobium powder containing appreciable amounts of both oxygen and carbon revealed a second mechanism of oxygen removal, involving the mutual elimination of these impurities as carbon monoxide.

High-temperature evolution of gas from compacts of such powders begins in the range 1600°–1700° C. As sintering proceeds, the outgassing rate decreases to an apparently low constant level. By prolonged sintering in this temperature range, a considerable reduction in carbon content can be achieved, provided that sufficient oxygen is also present. Sintering a powder compact containing 0.28 wt.-% carbon and a considerable excess of oxygen at 1700° C. for 24 hr. reduced the carbon content to <0.1 wt.-%. The oxygen remaining totalled 0.77 wt.-%, thus giving a product which was not workable.

The controlling factor in the rate of elimination of carbon probably depends to a large extent on the physical state of the compact, i.e. on the availability of free surfaces and open porosity which will permit the easy escape of volatile products. If sintering at 1700° C. was interrupted at an early stage and the material crushed, recompact, and resintered, gas evolution once again proceeded at a higher rate. The role of crushing and recompact was to restore the open porosity, thus permitting the easier removal of volatile products from the body of the compact. Increased temperature or increased rate of heating caused blistering and swelling of the compacts. Above 2100° C. these effects lead to gross distortion of the compact and the development of large cavities within the body. Fig. 2 (Plate XLIV) shows the effect of sintering at 2300° C. for 1 hr., a rectangular compact initially containing 0.28 wt.-% carbon and 0.6 wt.-% oxygen.

Blistering can largely be prevented by adopting slow heating rates between 1700° C. and the sintering temperature. Fig. 3 (Plate XLIV) shows a section of an identical compact after sintering at 2300° C. for about 3 hr. The heating rate from 1700° C. was of the order of 5° C./min. For larger specimens the heating rate must be further reduced, if blistering is to be avoided.

Further development of the two-stage sintering technique showed that a short ( $\frac{1}{2}$ -hr.) first-stage sinter could be performed in the temperature range 2000°–2100° C. when the slight distortion introduced by swelling and blistering did not cause any practical difficulties in the operation of either induction- or resistance-heating procedure. The compacts were then embrittled with hydrogen to permit crushing and were recompact before undergoing a second-stage sinter during which the temperature was raised to 2200°–2300° C. for 1–3 hr. During the final treatment, a major proportion of the excess oxygen is eliminated as a volatile oxide.

For efficient purification by the two-stage sintering technique, the proportion of carbon and oxygen present

required balancing. Experiments carried out by adding carbon to niobium powders of high oxygen content indicated that the optimum addition was approximately two-thirds of that theoretically required to combine with the oxygen present as carbon monoxide. It is probable that some of the oxygen is eliminated as a volatile oxide and that this accounts for the lower proportion of carbon required.

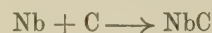
Batches of powder containing initially 0.3–0.5 wt.-% oxygen and 0.22 wt.-% carbon treated by this method were consolidated to ductile metal containing 0.002–0.004 wt.-% oxygen and 0.01–0.05 wt.-% carbon.

#### (d) Carbon

The carbon content of niobium powders produced by the  $K_2NbF_7$  method was of the order of 0.3 wt.-%, although in some early samples analyses of over 1.0 wt.-% were recorded. Carbon was a minor impurity in powder produced by the chloride method.

Carbon was unaffected by vacuum sintering, except by the carbon/oxygen reaction. As indicated in the preceding section, purification to <0.05 wt.-% was obtained by double sintering when a sufficient excess of oxygen was also present.

When carbon additions were used in the purification of powders of high oxygen content, metallographic evidence indicated that the reaction:



took place at temperatures below those at which carbon monoxide was formed.

#### (e) Other Impurities

The principal metallic impurities found in powders made by the  $K_2NbF_7$  method were iron (about 0.06 wt.-%) and silicon (about 0.06 wt.-%). Early samples of hydrogen-reduced powder were sometimes contaminated with other metals, e.g. chromium, nickel, molybdenum, arising from the structural materials used in the apparatus.

Except in the case of silicon, only slight reductions of such impurities took place during high-temperature vacuum sintering.

### 2. DENSIFICATION

The formation of dense, sintered metal of good mechanical properties took place simultaneously with purification, although, as indicated in previous sections, permanent mechanical damage was liable to occur under certain conditions of outgassing. With the introduction of a crushing stage, the major purification of the niobium powders was in effect carried out as a preliminary to the true powder-metallurgy fabrication of this metal. The metal made by sintering cold compacts of high-purity niobium powders was, however, a typical powder-metallurgy product, with 5–15 vol.-% porosity. Pure niobium in this form was ductile; during severe cold deformation little work-hardening was observed. Thin compacts could be rolled to 0.002-in. foil without intermediate annealing. However, porous metal was not suitable for fabrication under conditions of complex stress. To produce sound metal of virtually zero poros-



ity, it was necessary to cold forge the sintered bar in simple compression, and finally resinter to weld up the flattened pores.

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## II.—Development of a Commercial Sintering Process

### I.—INTRODUCTION

THE sintering of niobium *in vacuo* is a process during which both densification and purification occur to give ductile metal with a very low porosity. The most important impurity to be eliminated is oxygen, since this causes the hardness and brittleness which prevent successful working of the metal to sheet, rod, wire, &c.

Oxygen is removed either by volatilization at 2100°–2300° C. as niobium oxide (probably a lower oxide), or alternatively as carbon monoxide in the range 1700°–1900° C. In practice, both processes occur, but it is advantageous to add carbon to the metal powder before sintering, in an amount dependent on the oxygen content, so that the greater part of the oxygen is removed as carbon monoxide, only the last traces being removed as niobium oxide. Any silicon present in the metal is also removed in the temperature range 1700°–1900° C., presumably as silicon monoxide, which is known to be volatile under such conditions.

There are three main reasons for preferring to eliminate oxygen as carbon monoxide. In the first place the loss of valuable niobium is greatly reduced from 5 to 1 wt.-% and, secondly, the sintering time required to produce a soft bar is considerably shortened owing to the fact that the alternative oxide-evolution process is slow, if the bar is to retain its shape. In the case of tantalum, the sintering temperature (about 2600° C.) is well above the oxide-evolution temperature, and thus the volatilization rate is high. However, since niobium melts at 2460° C., the temperature of oxide evolution cannot be allowed to rise above 2300° C., and as a consequence the volatilization rate is low. Thirdly, the removal of oxygen as carbon monoxide is preferable, in view of the fact that oxygen causes a depression in the melting point.\* This phenomenon sets a limit to the temperature at which the oxygen can be removed; as purification takes place, the temperature may be increased.

In practice, the temperature of the bar is gradually raised to about 1800° C. and the pressure rises owing to rapid evolution of carbon monoxide. When the majority of the gas has been evolved and the pressure drops, the temperature is raised further in small steps to 2300° C. This temperature is maintained for about 6 hr. to remove substantially all the oxygen and to complete the final

stages of densification. Between 1800° and 2300° C., the heating rate is kept low to avoid any possibility of "blowing up", caused by gas evolution at the centre of the bar coupled with rapid densification at the surface.

Either the direct resistance-heating method—where the bars are heated by the passage of current through them—or the induction-heating method may be used. Their advantages and disadvantages will not be discussed in detail here, but it may be noted that the chief advantage of the induction method is the saving of material that results from the absence of unsintered ends, inevitable in the direct-resistance method, and that the major saving in the direct-resistance method is that cheaper equipment may be used. The induction method of heating was chosen by Murex, Ltd., in a collaborative programme in which the Research and Development Branch of the U.K.A.E.A., Springfields, concentrated their efforts on resistance-heating methods.

### II.—EXPERIMENTAL

The sintering of niobium was carried out in a high-vacuum, H.F., type V.S.G. 10 induction furnace made by Gerätebau-Anstalt, Balzers, Liechtenstein, which has a tank capacity of 200 l. The furnace case was evacuated by a diffusion pump backed by a rotary pump, and an ultimate pressure of  $10^{-5}$  mm. of mercury was obtainable. The electrical equipment providing power for H.F. induction heating was a motor generator set with a maximum output of 50 kW. at a frequency of 10 kc./s. The furnace set-up is shown in Fig. 4 (Plate XLIV).

In the high-frequency induction method the bar to be sintered is placed in a heating cylinder made of tungsten and the latter is placed concentrically in a high-frequency induction coil. The bar is heated by radiation from the heating cylinder. The apparatus used for sintering niobium by H.F. induction heating *in vacuo* is illustrated in Fig. 5 (Plate XLIV).

To make the most efficient use of the power induced, a system of radiation screens is necessary. Molybdenum has been found to be the most satisfactory material for these screens. In all cases the cylinders and discs of the screening apparatus are split in such a way that no complete paths are presented for the closed-circuit flow of induced eddy currents. In this way the majority of the

\* This probably accounts for the low values given for the melting point of niobium in less recent times.

power goes to heating the bar, and losses by radiation from the susceptor are cut down by back reflection from the surface of the molybdenum screens. The screens are isolated from the coil and from each other by a silica sleeve and the coil is water-cooled. The tungsten cylinder extends beyond the base of the coil, clear of the more intense parts of the field, and rests in a carbon block standing on the water-cooled base of the furnace.

The bar to be sintered is pressed from a mixture of degassed virgin powder and degassed hydrided niobium scrap containing the amount of additional carbon calculated from the oxygen content of the composite. The addition of hydride is not essential to the sintering process, but is necessary economically in that it allows the recovery of clean scrap such as sheet cuttings, &c. The addition is, however, advantageous in that the hydride increases the overall purity (because this material has already been purified during the first sintering process) and coarseness of the bar when mixed with sodium-reduced powder. This facilitates purification and the removal of gases, thus enabling a more rapid heating rate to be used without any danger of "blowing up". Hydride and virgin powder are pretreated at 1100° C. *in vacuo*, to remove all physically absorbed gases. These are undesirable in the pressed state, since they tend to cause pressure cracks and are evolved violently on heating up and produce more cracks or even disintegration.

About 750 g. of the mixture is pressed at 30 tons/in.<sup>2</sup> to give a bar  $7 \times 2\frac{3}{8} \times \frac{5}{8}$  in. The bar is placed in the heating cylinder and as far as possible is separated from it by sheet or wire. The temperature inside the susceptor is measured optically through a double silica window in the furnace lid and through holes in the top set of radiation screens and the susceptor lid. The necessary corrections for the optical effects of the window and any deposited films are made by comparison with a standard reference filament made from tantalum tape. The top of the bar is radiating approximately as a black body, as it is completely surrounded by the heating cylinder and lid.

In practice, it is more convenient to control the sintering by means of the power-input readings. The appropriate power schedule is first obtained from a graph relating power and temperature up to 2300° C. This schedule is such that a temperature of 1700° C. is attained in 40 min. and the bar is then maintained between 1700° and 1900° C. for 2 hr. until most of the carbon monoxide and silicon monoxide have been evolved. The power is then gradually raised over a period of 6 hr. until a temperature of 2300° C. is reached. After 6 hr. at 2300° C., the oxygen not removed by the carbon is volatilized as niobium oxide and sufficient densification is ensured for working of the ductile bar. During the sintering operation, the pressure varies, reaching a maximum of  $0.4 \times 10^{-3}$  mm. at the outgassing stage, this being finally reduced to  $2 \times 10^{-5}$  mm. at completion of purification.

The linear shrinkage after sintering at 2300° C. for 6 hr. is about 15% and the hardness about 75 V.P.N. (30-kg. load) at a density of 8.0 g./c.c. (93% of the theoretical density, namely, 8.57 g./c.c.).

If the thickness of the bar to be sintered is greater than about  $\frac{5}{8}$  in., the sintering time becomes excessive. It is

quicker to reduce the thickness by about 30% by cold rolling after sintering for the normal length of time and then to resinter, rather than to extend the primary sintering cycle. Resintering for about 4 hr. at 2300° C. ensures complete purification of the bar. After this double sinter operation, the hardness of the niobium is about 85 V.P.N. at a density of 8.4 g./c.c. (98% of the theoretical value).

### III.—RESULTS

As discussed in the first part of this paper, the sintering process for niobium results not only in densification but also in purification. Oxygen is the main impurity eliminated during sintering—from approximately 0.5 wt.-% in the powder to 0.05 wt.-% in the sintered metal. This reduction in oxygen is paralleled by a reduction in the carbon content to <0.01 wt.-%. The carbon content in the original powder is of the order of 0.2 wt.-%, but more may be added before sintering, depending on the oxygen content of the powder. Silicon present in the original powder to the extent of about 0.1 wt.-% is removed during sintering, presumably as silicon monoxide, to give a final content of <0.01 wt.-%. Nitrogen is reduced during vacuum sintering from approximately 0.1 wt.-% to values approaching 0.01 wt.-%. The only other major impurity removed during sintering is lead. This may be present, initially, in amounts up to 0.1%, but is reduced in the final bar to the order of 0.005 wt.-%. Table I shows a typical analysis of virgin powder compared with sheet rolled from sintered bar.

TABLE I.—Typical Analysis of Virgin Niobium Powder and Sheet Rolled from Sintered Bar.

	Powder	Sheet
	wt.-%	wt.-%
C . . . . .	0.25	<0.01
O . . . . .	0.5	0.05
N . . . . .	0.07	0.01
Ta . . . . .	0.3	0.3
Si . . . . .	0.08	<0.01
Fe . . . . .	0.05	0.05
Pb . . . . .	0.1	0.005
Ti . . . . .	0.05	0.05
Sn . . . . .	0.08	0.08

Ductile sintered bars can be cold rolled to sheet 0.02 in. thick without annealing (about 95% reduction). The hardness of annealed sheet varies from 80 to 120 V.P.N., and the density is equal to the theoretical value. The sheet can be deep drawn to tubes and spun to symmetrical shapes. Ductile niobium bars with a square cross-section can be swaged to rod, and small-gauge rod can be drawn to wire. Process anneals are carried out at suitable intervals to prevent too much work-hardening. The metal is easily welded by both the resistance-welding method and by the normal argon-arc technique, provided that the necessary protection is given to the weld area.

### ACKNOWLEDGEMENTS

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# THE PRODUCTION AND FABRICATION OF MASSIVE NIOBIUM METAL \*

1759

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## SYNOPSIS

An account is given of two possible methods—(i) melting and (ii) compacting and sintering—for producing massive ductile niobium from the powder obtained by reduction processes. Both methods demand the use of temperatures over 2000° C. and a high vacuum to minimize contamination and promote the removal of impurities. The powder-metallurgy technique offers the more promising possibilities, and a detailed description is given of the methods of processing developed by the U.K. Atomic Energy Authority. In conclusion, reference is made to the cold-working and welding properties of ductile niobium.

## I.—INTRODUCTION

THE general considerations leading to a decision to develop niobium as a possible canning material for use in nuclear reactors, and the principles underlying the production of the metal in a massive ductile form, have been dealt with elsewhere.<sup>1,2</sup> The main purpose of the present paper is to give a more detailed account of the application of these principles to the development of production techniques, and to describe the processes for subsequently fabricating the metal to sheet, rod, tubes, and other shapes.

A number of methods have been proposed for the production of the metal, including the electrolysis of fused potassium niobium oxyfluoride, the reduction of the oxide by the carbide,<sup>3</sup> and the reduction of potassium niobium heptafluoniobate by metals such as sodium and magnesium.<sup>4</sup> The reduction of the trichloride by hydrogen and other reductants has also been suggested.<sup>5,6</sup> All these methods yield the metal in powder form, and the two major problems in further processing are to remove deleterious impurities and to convert the powder into massive form.

The two types of processing suitable for the production of massive ductile metal are: (i) melting and (ii) powder-metallurgy methods. In both cases temperatures in excess of 2000° C. must be used, and a high standard of vacuum technology is demanded to minimize contamination by traces of oxygen and nitrogen; in addition, provision must be made for exposing as large a surface area as possible in order to expedite the elimination of impurities.

## II.—MELTING TECHNIQUES

The use of conventional H.F. melting methods is normally restricted to temperatures of the order of 1700° C. Above this limit, particularly when dealing with reactive metals such as niobium, the refractory problem becomes acute both from the point of view of

the high standards of purity required, and the strength of the lining material at operating temperatures. This restricts the possible processes to arc-melting techniques, the two principal variants of which are: (a) the use of non-consumable tungsten or thoriated tungsten electrodes and (b) the use of consumable electrodes built up of niobium powder pressed into convenient shapes.

If the non-consumable electrode process is used, the metal is liable to suffer contamination from the electrodes. Moreover the need to maintain a small pressure of an inert gas such as argon in order to ensure a stable arc means that the purification process will certainly be retarded, and it may be inhibited altogether. Prolonged treatment in specially designed equipment, in which provision is made for circulating and purifying the inert gas, would be necessary in order to achieve effective purification in a reasonable time.

In the consumable-electrode process, the mass and size of the ingot produced may be varied within wide limits. However, the time interval between melting and solidification is very short, thus providing only limited opportunity for the removal of impurities in gaseous form. The volatilization of impurities, such as oxides of niobium, may not prove effective for their removal, as the vapour will condense on the walls of the water-cooled mould and be partially or completely reabsorbed in the metal as melting proceeds. To achieve a satisfactory result, the carbon and oxygen would have to be present in exactly the right proportions to make possible their removal in gaseous form. Lack of accurate data renders the calculation of the equilibrium pressures of carbon monoxide over the molten metal very uncertain. However, it is possible that the reaction would proceed at the pressures attainable in commercial arc-melting equipment. If such a unit were operated at a chamber pressure of  $10^{-2}$  mm. Hg, the pumping speed required for the removal of 0.3% carbon as carbon monoxide at melting rates of 2 kg./min. would be of the order of  $10^4$  l./sec.

The practicability of removing sufficient of the impurities to give a truly ductile product, using either

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variant of the arc-melting process, has not been established. The method can, however, certainly be applied to the production of large masses by melting niobium rendered ductile by other methods.

Mention may be made at this point of the possibility of employing electron-bombardment techniques for the production of ultra-pure material. This technique has been developed on a laboratory scale at the Culcheth Laboratories of the U.K.A.E.A., and it has been shown that exceptionally high degrees of purity can be achieved. Methods of increasing the scale of operation are at present being investigated.

### III.—POWDER-METALLURGY TECHNIQUES

#### 1. METHODS OF HEATING

The alternative method of processing niobium is by the use of powder-metallurgy techniques, in which the metal is retained in the solid phase. The operating temperatures are rather below the melting point of the metal, and the removal of impurities in both gaseous and vapour form is practicable. The necessary energy for raising the bar to temperature can be supplied by induction or resistance heating (direct or indirect).

The fact that temperatures in excess of 2000° C. are required and the need for restricting contamination, particularly by carbon, rules out the use of conventional molybdenum or tungsten cage-type furnaces, and the use of graphite resistors for indirect heating.

Rapid advances are now being made in the development of both apparatus and techniques for high-frequency vacuum sintering. Only motor generators are suitable for supplying the low-voltage input required for operation in high vacuum. The frequencies preferred are of the order of 2-4 kc. and the voltage should not exceed 250 V. in order to minimize difficulties arising from glow discharge. One of the problems associated with the use of induction heating arises from the fact that variations of temperature along the length of the specimen, i.e. along the major axis of the inductor coil, cannot be directly detected. This is probably not of primary importance from the production aspect; provided that the necessary conditions can be established and maintained precisely for each metal or alloy on the basis of experience, the measurement of the top temperature may be adequate as a means of control.

The direct-resistance heating method, in which the source of energy is the passage of an electric current through the specimen, was first developed by Coolidge in 1909 and used for the sintering of molybdenum and tungsten in hydrogen atmospheres. A logical development has been the adaptation of the equipment to permit of vacuum processing. Equipment is commercially available, the design of which is based on many years' operating experience. The method is particularly suitable for development work, as the equipment can be so designed that the bar may be examined visually over its whole length throughout the processing cycle. The use of water-cooled electrodes for gripping the bar has the disadvantage that a temperature gradient is developed at both ends; this may be partially offset by arranging for suitable changes of cross-sectional area, but some discard is inevitable.

Summarizing, it may be said that both induction and

resistance heating are practicable for the sintering of niobium using powder-metallurgy methods, and the decision as to the choice of method is dependent on a number of factors, including the availability of equipment and of processing facilities. Arc-melting techniques need further development, but the possibilities of the method improve as the purity of the raw powder increases. Given a sufficiently pure starting material, there is no reason why this method, with its enormous potential output, should not prove to be the most economical, particularly where part of the capacity of an existing unit can be made available.

#### 2. POWER REQUIREMENTS FOR SINTERING

The power required for sintering is a function of the surface area of the specimen, the temperature required, and the surface emissivity of the specimen, and is approximately 60 kW. for a specimen  $24 \times 4 \times 1$  in., of surface emissivity 0.4 radiating freely at 2000° C. The use of heat-reflecting screens would reduce this figure considerably. The power required increases linearly with surface emissivity.

In the case of resistance heating, it is essential that the electrical system be designed to supply the power required over a wide range of voltages and current values, as the electrical resistivity decreases by a factor of over  $10^3$  during sintering (see Fig. 4, p. 390). The maximum supply voltage will be that necessary to ensure that sufficient amperage can be passed to permit of heating the bars in the "green" condition. The maximum current values are associated with the end of the process, when the bar is in the purest condition at maximum temperature.

The amperage required to maintain rectangular specimens of the same material but of differing widths and thicknesses at the same temperature may be derived to a first approximation from the relationship:

$$I^2 = kwt(w + t)$$

where  $I$  = current required,  $w$  = width of bar,  $t$  = thickness of bar and  $k$  = constant.

It will be noted that the amperage required is independent of the length of the specimen.

#### 3. VACUUM REQUIREMENTS FOR SINTERING

Niobium metal, particularly in powder form, is an excellent "getter", rapidly absorbing both oxygen and nitrogen when heated; in addition, hydrogen is rapidly absorbed at temperatures up to 500° C. All three elements, together with carbon, are present in appreciable amounts in the as-reduced powders.

The elimination of these impurities is vital to the production of the ductile metal, and the successful application of high-vacuum techniques is a major controlling factor at all stages involving processing at elevated temperatures. The vacuum requirements have therefore been considered in some detail, on the assumption that the rates of diffusion of the impurities to exposed surfaces do not constitute the controlling variable for their elimination.

O'Driscoll and Miller<sup>2</sup> have shown that three main purification mechanisms may operate during sintering. First, there is the low-temperature elimination of



hydrogen up to 1000° C. This is followed by the formation of carbon monoxide above 1650° C., and, lastly, the elimination of oxygen takes place at temperatures above 1900° C., probably as the result of the volatilization of an oxide of niobium. The vacuum requirements are different for each stage of processing.

The hydrogen released at low temperatures gives the largest gas flow of the whole sintering cycle, and large pumps are required, first, to permit of its rapid removal, and secondly, to return the system to the pressure at which the subsequent stage of purification can proceed. Care must be exercised at the early stages of gas removal to avoid the mechanical disruption of the bar, owing to the build-up of excessive internal pressures of hydrogen. Important factors are the rate of temperature rise, which controls the rate of evolution of gas at the surface of individual particles and the pressing pressure used, and the particle-size distribution of the powder, both of which control the permeability of the compacts. The thickness of the compacts is also important. It should be stressed that cracks or other flaws which develop at this stage are difficult, if not impossible, to eradicate at later stages of processing. The vacuum requirement for this operation is clearly a large volume capacity at a reasonably low pressure.

The next stage of gas evolution is associated with the formation and removal of carbon monoxide. Richardson<sup>7</sup> estimates the equilibrium pressure at 2000° C. to be given, within a factor of ten, by:

$$P_{\text{CO}}(\text{mm. Hg}) = 3 \times 10^{-2} (\text{wt.}\% \text{O}_2)(\text{wt.}\% \text{C}),$$

from which it may be shown that the partial pressure of carbon monoxide in the system must be maintained below  $3.4 \times 10^{-5}$  mm. Hg to permit of the reduction of both carbon and oxygen to less than 0.03%. The pumping speed required to remove the carbon in a given time can also be calculated and gives a value of 7 l./sec./g. of niobium sintered for a reaction time of 5 hr. The result is, however, of little practical value, as the uncertainty of the thermodynamic data is such that this value could vary between 0.7 and 70 l./sec./g. The pumping speed is, therefore, best considered in relation to an actual experimental result. Fig. 1 shows the pressure/time relationship obtained for the sintering of a 2-kg. niobium bar in a system having a rated pumping speed of the order of 6500 l./sec. The rapid increase of pressure following the initial removal of hydrogen will be noted. The second increase of pressure, which begins at 1650° C., is associated with the removal of carbon monoxide. The agreement between the calculated and observed values of the partial pressure of CO, at the beginning and end, respectively, of the carbon-monoxide evolution is worthy of comment. The time required to complete the sintering was, in this instance, 6 hr., the bar thickness being 0.9 in.

Little information is available regarding the vacuum requirements for the third reaction, i.e. the elimination of oxide as vapour. Clearly the reaction is primarily dependent on the vapour pressure of the oxide. A lower limit of pressure can be specified on the basis that no increase in reaction rate can be expected when the mean free path in the system exceeds the distance between the specimen and the walls of the chamber, which corresponds to  $3 \times 10^{-4}$  mm. Hg for a distance of 25 cm. Any oxygen "seen" by the niobium will react to form oxide,

and this will effectively decrease the rate of oxygen removal; leak rates must therefore be kept to a minimum.

The object of using high pumping speeds is to facilitate the elimination of impurities. However, all oil-diffusion pumps suffer from a tendency for the "back-streaming" of oil vapour. This is normally minimized by introducing systems of baffles which may or may not be refrigerated, depending on the contamination that can be permitted.

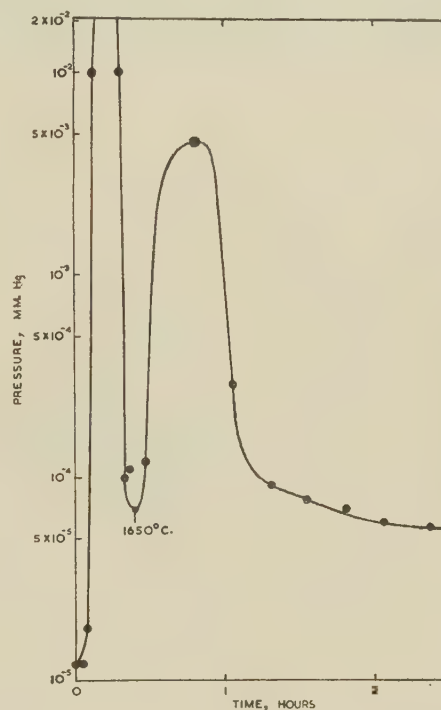


FIG. 1.—Pressure/Time Relationship for the Sintering of Niobium.

These baffles reduce the rated pumping speed, and the more effective the baffle, the greater is this effect. This factor should be taken into account in assessing the size of pumps required for any particular system. The same principle applies to all other forms of shielding between the pump and the specimen, e.g. heat-reflecting screens, and the aim in designing the equipment should be to ensure the maximum effective pumping speed at the surface of the specimen.

In conclusion, it may be stated that niobium has been successfully sintered in equipment having an ultimate vacuum of  $1 \times 10^{-5}$  mm. Hg, using oil-diffusion pumps with a rated speed of 3 l./sec./g. of material sintered. Theory predicts that if the partial pressure of CO in the system could be decreased, then the oxygen and carbon contents could be brought to lower values; in practice, this would depend on the ability of the system to remove the additional carbon monoxide at a reasonable rate at these lower pressures and would be effected by using larger pumps than at present.

The leak rate of the system is of primary importance, as it controls the effective rate of removal of oxygen as oxide vapour. Recent tests, in which specimens were sintered for consecutive periods of 2 hr., showed that when an abnormal leak developed, the hardness of the bar after treatment increased from 70 to 100 V.P.N.

The hardness decreased to its original value after re-treatment under normal conditions.

4000 amp. at 30 V. or 8000 amp. at 15 V. Current control is effected by means of an aut regulating transformer.

#### IV.—EQUIPMENT

##### 1. SINTERING UNIT

The equipment used for development work at Springfield is of the direct-resistance heating type and is shown schematically in Fig. 2. It consists essentially of a sintering bell, a vacuum-pumping unit, a transformer system, and a suitably integrated control system.

The sintering bell is a double-walled copper chamber,

##### 2. TEMPERATURE MEASUREMENT

The accurate and reproducible measurement of temperature is of particular importance during the later stages of sintering, when the bar is maintained for some hours at a temperature near the melting point of the metal. The instrument used is a disappearing-filament type of optical pyrometer sighted through either of the quartz observation windows. A correction is applied for the absorption of the window.

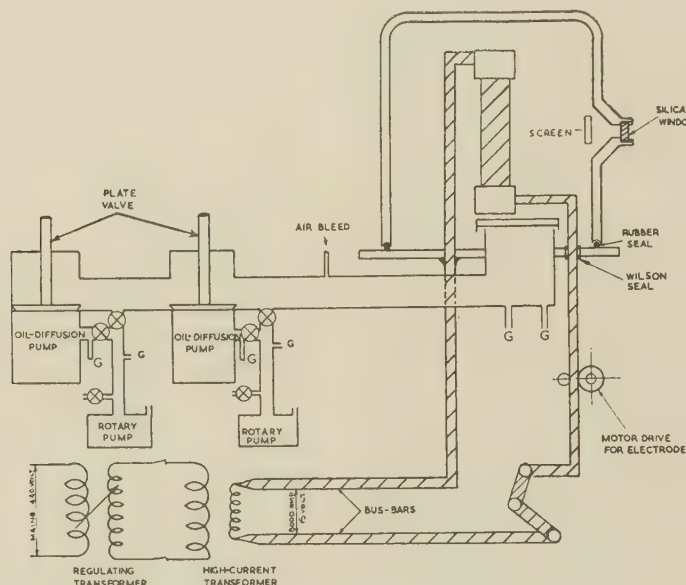


FIG. 2.—Schematic Diagram of Sintering Unit.

approximately 2 ft. in dia. and 3 ft. high, having two observation ports fitted at right angles to one another, thus enabling both the front face and edge of the bar being sintered to be viewed. Each port is fitted with a mechanism by means of which a number of glass slides or a blank plate can be rotated in turn to cover the inside surface of the window. The base plate is fitted with a central port which connects to the pumping system, and the vacuum seal between the bell and base plate consists of a trapezoidal-section rubber ring. The conductor system supplying current to the bar is mounted on the base plate, and the system is arranged to permit of compensation for shrinkage during sintering. The water-cooling system is divided into five separate circuits for the bell, base plate, upper and lower electrode, and the diffusion pumps, respectively.

The vacuum unit consists of two 14-in. oil-diffusion pumps fitted with water-cooled baffles and having a combined pumping speed (unbaffled) of 6500 l./sec. at  $10^{-4}$  mm. Hg. Each diffusion pump is backed by its own rotary pump, giving two systems which can be operated either together or independently, as may be required. The ultimate pressure attainable in the system is of the order of  $1 \times 10^{-5}$  mm. Hg.

The current for sintering is supplied by a high-current transformer which can be connected to supply either

Two major difficulties have been encountered: first, the recording of temperatures lower than the true values as a result of the deposition of volatiles such as niobium oxide on the inner surface of the observation windows, and, secondly, inaccuracies arising from variations in surface emissivity. The importance of the emissivity correction will be appreciated from the fact that for a true temperature of  $2300^{\circ}\text{C}$ . the observed temperature varies from  $2220^{\circ}\text{C}$ . for  $\epsilon = 0.75$  to  $2020^{\circ}\text{C}$ . for  $\epsilon = 0.35$ .

The clouding of the observation windows cannot be completely prevented, but may be minimized by introducing suitable baffles and reducing both the number of observations taken and the time per observation to a minimum.

The emissivity of niobium can be calculated from temperature measurements made in, and immediately adjacent to, a hole having a depth:diameter ratio of 5:1 drilled in the specimen before sintering. The spectral emissivity may then be calculated from the relationship:

$$\log_{10} \epsilon_{\lambda} = K \left( \frac{1}{T_1} - \frac{1}{T_2} \right),$$

where  $\epsilon_{\lambda}$  = spectral emissivity for wave-length  $\lambda$ , and  $T_1$  and  $T_2$  are the "hole" and surface temperatures, respectively, measured through a filter restricting the



wave-length of light passing to  $\lambda$ . Fig. 3 shows the variation in spectral emissivity ( $\lambda = 6500 \text{ \AA}$ ) for a niobium specimen during the course of an actual sintering operation. The fall in emissivity as sintering progresses should be noted.

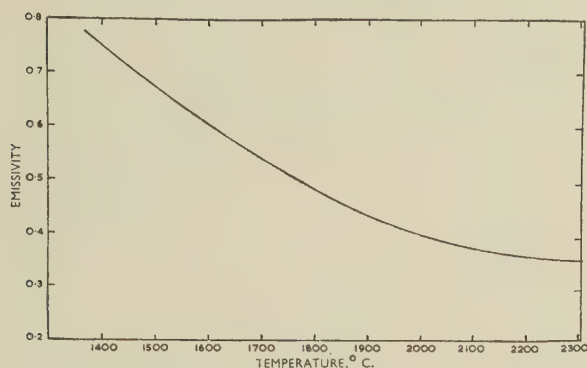


FIG. 3.—Variation of Spectral Emissivity with Temperature During the Sintering of Niobium Powder Compacts. ( $\lambda = 6500 \text{ \AA}$ .)

## V.—PROCESSING TECHNIQUES

### 1. SINTERING

The first mechanical operation is to prepare the requisite mixture of recirculated and raw powder. The reasons for mixing the two grades will be made clearer later. The mixture is then pressed into bars of square or rectangular section, depending on whether the material is required for rod or sheet. The maximum bar dimensions to which niobium can be sintered depend on the power and current available, and for the equipment being considered are  $18 \times 2\frac{1}{2} \times 1$  in. Particular care must be taken to ensure that the die design and method of pressing permit the load to be simultaneously released on all faces of the compact, in order to minimize the tendency for lamination to occur. Defects arising from the pressing operation cannot be eradicated during the later stages of processing.

The pressed, or "green" bar, as it is sometimes called, is charged into the sintering unit, the assembly is evacuated, the unit checked for leak rate, and the power switched on. The temperature is raised gradually to  $300\text{--}400^\circ \text{C}$ ., held for a short time whilst most of the hydrogen is evolved, and then increased to approximately  $2300^\circ \text{C}$ .; the total heating time to this temperature is about 40 min. Most of the shrinkage occurs in the temperature range  $1600\text{--}2000^\circ \text{C}$ ., and must be compensated for by adjustment of the electrode positions. The temperature is then further raised to the final temperature, which is of the order of  $2300^\circ \text{C}$ . The selection of the final sintering temperature depends primarily on the bar thickness, because a temperature gradient extends from the outside to the middle of the bar, the temperature of the centre being the higher. The sharpness of the gradient increases as the thickness of the work-piece increases and has been estimated to be of the order of  $50\text{--}80^\circ \text{C}$ . for a thickness of 0.9 in. Since it is not permissible for melting to occur, the maximum temperature as measured on the outside surface must be decreased as the thickness increases; conversely thinner compacts can be taken to higher

overall temperatures. The time at maximum temperature may vary between 2 and 10 hr., depending on the mass of material being sintered. The bar is then allowed to cool to  $200^\circ \text{C}$ . before the vacuum is broken.

The next operation is to reduce the thickness of the sintered bar by 25–30%, using a cold-forging technique. The bar is then resintered, and in this condition the temperature may be raised very rapidly to the maximum value of  $2300^\circ \text{C}$ .; both temperature and time at temperature are dependent on the mass and thickness of the bar being treated.

The ends of the bar are then removed and the material rolled to sheet, or swaged to bar, as required.

### 2. REMOVAL OF IMPURITIES DURING SINTERING

The work described in this paper has been confined to the results obtained using powder supplied to the U.K.A.E.A. by Murex, Ltd., Rainham. The chemical composition of a number of separate batches of powder is given in Table I. The principal non-metallic impurities are oxygen, hydrogen, and carbon, with silicon and iron as the main metallic impurities. The true particle-size distribution of the powder, as determined by the electron microscope, is in the range  $0.01\text{--}5 \mu$ . Normal sedimentometer methods, however, give the range as  $1\text{--}50 \mu$  presumably on account of aggregation. The powder is stable and stores well.

Preliminary sintering tests with the powder proved unsuccessful owing to the formation of blisters, which,

TABLE I.—Chemical Composition of Niobium Powder.

Batch No.	Weight-%					
	O <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	C	Fe	Si
1	0.47	0.05	0.30	0.28	0.03	0.10
2	0.62	0.03	0.29	0.22	0.03	0.04
3	0.62	0.04	0.34	0.25	0.05	0.09
4	0.67	0.05	0.26	0.31	0.05	0.06
5	0.66	0.08	0.26	0.30	0.05	0.03
6	0.74	0.06	0.27	0.30	0.05	0.05
7	0.77	0.05	0.30	0.23	0.05	0.06
8	0.53	0.04	0.23	0.31	0.05	0.08
9	0.54	0.07	0.22	0.32	0.06	0.04
10	0.25	0.06	0.21	0.30	0.02	0.05

on examination, were found to be due to the development of gross internal cavities. These cavities were associated with the development of internal gas pressures, subsequent to the closure of surface voids by sintering.

At the same time, work was proceeding on the development of recirculating techniques based on embrittlement by hydrogen. This gave a relatively coarse grade of powder at one of the intermediate crushing stages. Tests made on this powder showed that a high proportion of open porosity remained after sintering at  $2300^\circ \text{C}$ ., and that the bars were completely free from the tendency to blister even when heated rapidly.

This work forms the basis of the procedure now in use, the aim being to adjust the particle size by mixing the two grades of powder to give the required characteristics. The photomicrographs shown in Figs. 7 and 8 (Plate LXV) illustrate the abnormally high degree of porosity remaining after the first sintering treatment, and should

be compared with Fig. 9 (Plate LXV), which shows the structure of the material after working and annealing.

Table II gives the chemical composition of a number of bars before and after sintering. The hydrogen content is not reported, but was in all cases less than 0.001%.

TABLE II.—Change of Chemical Composition of Niobium Powder on Sintering.

Chemical Composition of Powder, wt.-%					Chemical Composition of Sheet, wt.-%				
O <sub>2</sub>	N <sub>2</sub>	O	Si	Fe	O <sub>2</sub>	N <sub>2</sub>	C	Si	Fe
0.71	0.09	0.18	0.03	0.04	0.005	0.006	0.001	0.007	0.03
...	...	...	...	...	0.01	0.013	0.015	0.007	0.05
...	...	...	...	...	0.018	0.002	0.02	0.007	0.03

It will be noted that there is relatively little change in the iron values, that the silicon content tends to be rather lower, and that the carbon, oxygen, and nitrogen contents are greatly reduced.

The rapid release of carbon monoxide at 1650° C. suggests that the diffusion of both elements in niobium is very rapid at this temperature, and gives added support to the suggestion that the controlling variable for carbon elimination is associated with the pumping speed available at the appropriate pressure.

The fact that two mechanisms for oxygen removal operate simultaneously means that the oxygen content of the initial powder must be greater than the stoichiometric amount required for the formation of carbon monoxide, if sufficient is to be retained for removal of carbon. No particular difficulties have been experienced

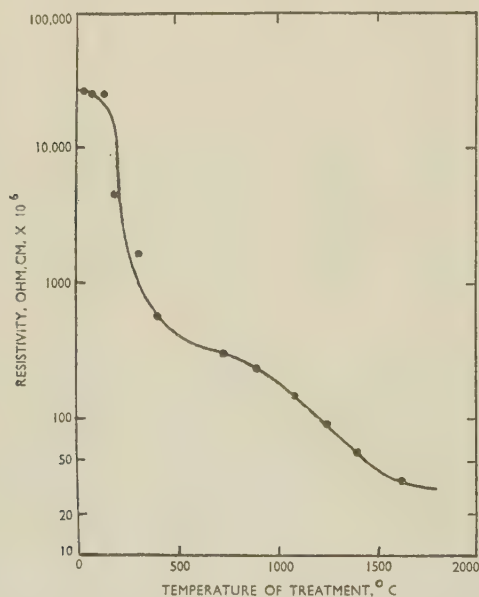


FIG. 4.—Variation of Resistivity of Niobium Compacts After Heat-Treatment at Temperatures up to 1600° C.

attributable to lack of sufficient oxygen for this purpose, although oxide additions could, of course, easily be made if the sintered bars were found to have high carbon contents.

### 3. PHYSICAL CHANGES DURING SINTERING

Not unexpectedly, the resistivity of niobium on sintering drops progressively on heating and has decreased by a

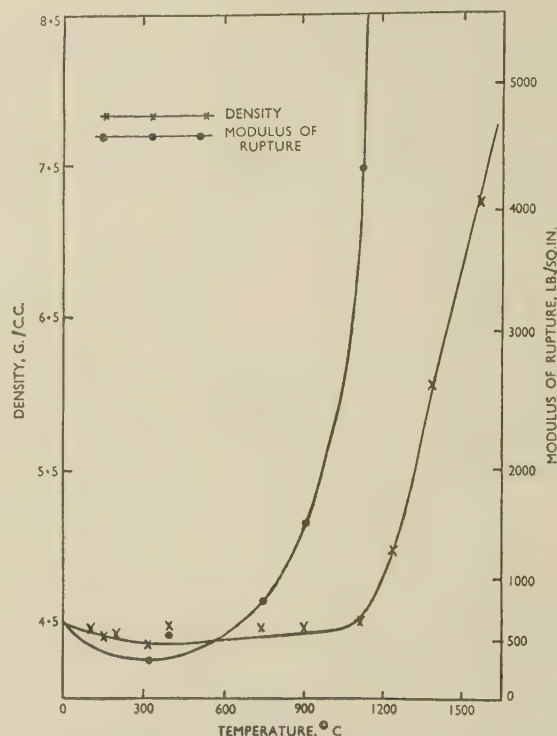


FIG. 5.—Change in Density and Modulus of Rupture of Cold-Pressed Niobium Compacts Heated for 4 Hr. at Temperatures up to 1600° C.

factor of  $10^3$  after heating to 1600° C. The values given in Fig. 4 were determined at room temperature after treatment and refer to the original powder as received from Murex, Ltd. The changes in density and modulus of rupture for compacts sintered at temperatures up to 1600° C. are shown in Fig. 5. It will be noted that the strength of the compact shows a small initial decrease, after which, starting at approximately 350° C., it increases rapidly. This suggests that diffusion processes are operating even at these low temperatures. The density results are rather more erratic at low temperatures, but the trend towards increasing density at temperatures above 900° C. is quite clear. Here again, the results refer to the "fine" grade of powder as received from Murex, Ltd. Table III gives the density of bars processed by the current technique, using a mixture of coarse and fine powder.

The hardness of porous bodies, such as sintered bars, does not give an accurate assessment of their mechanical properties, required in this instance for evaluating the success or otherwise of the sintering operation. Hardness tests on sintered bars are thus of very little value and are not generally made. However, the hardness test is of use, as a basis for comparison, for bars in the forged and resintered condition, and values of the order of 120 V.P.N. are normally recorded after a reduction of 25% of the cross-sectional area by cold forging. This figure drops to the range 60-80 V.P.N. on resintering.



Further cold working, such as rolling, results in a steady increase to a value of the order of 160 V.P.N. The

impracticable, to re-treat components during fabrication at temperatures sufficiently high to ensure the removal of impurities such as oxygen and nitrogen.

TABLE III.—Density Changes in Niobium During Processing from Powder to Sheet.

	Density, g./c.c.
Reported metal density . . . .	8.6 *
True powder density :	
(a) As-reduced condition . . . .	7.9
(b) After recycling . . . . .	8.4
Bar after pressing at 12 tons/in. <sup>2</sup> . . . .	5.5
After sintering . . . . .	7.0
After forging . . . . .	8.2
After resintering . . . . .	8.3
As sheet . . . . .	8.6

\* As given in ref. 8.

relationship between hardness and degree of cold work for fully annealed sheet, is shown in Fig. 6.

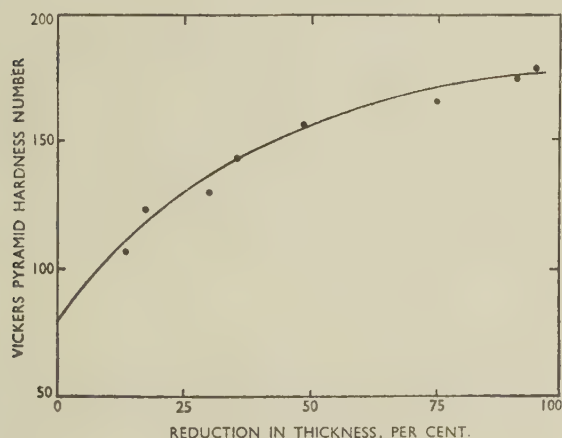


Fig. 6.—Relationship between Hardness of Niobium and Percentage Reduction in Thickness on Rolling.

#### 4. STRESS-RELIEVING

The niobium sheet, produced as described above, is extremely ductile, and can be rolled directly from sintered bar, say,  $\frac{1}{2}$  in. thick, to thin (0.005 in.) strip without any intermediate stress-relieving operations. However, certain mechanical-working operations, of which cupping is a good example, introduce complex stresses which can lead to rapid failure by cracking at the lip of the cup, and it has therefore been necessary to devise suitable methods for stress-relief.

Essentially, the technique consists of heating the sheet to temperatures in the range 1000°–1250° C. in high vacuum, holding at this temperature for some minutes, and then of allowing to cool in vacuum. All the conventional heating methods may be used, but H.F. techniques have a definite advantage, as rapid heating and reasonably short cooling times can be attained. The major factor in the design of suitable equipment is to ensure the lowest leak rate possible. This is particularly the case for shapes which require a number of heat-treatments, as the pick-up of impurities is cumulative. It is normally undesirable, and in most cases

## VI.—COLD-FORMING OPERATIONS

### 1. SHEET AND TUBE

The ductility of the metal is closely associated with its purity, and it is essential that forming operations shall be carried out entirely in the cold, unless the exclusion of all contaminating gases can be guaranteed during processing.

The following comments are restricted to processes actually used during the past two years and are representative of experience gained, rather than of the inherent formability of the metal.

Sheet can be rolled without difficulty on rolling mills of conventional design. Up to the present time the thinnest strip rolled has been 0.004 in., but there is no reason why foil as thin as 0.001 in. or less should not be produced, given suitable equipment.

The production of tubes by cupping and drawing begins with the blanking of discs having a suitable thickness : diameter ratio, and work done so far has used ratios varying from 1 : 48 to 1 : 60. The initial stages consist of cupping and drawing the discs on a hydraulic press. The percentage reduction in these cupping and drawing operations varies between 47.5 and 51% on the basis of the formula :

$$\left( \frac{D_b - D_p}{D_b} \right) \times 100,$$

where  $D_b$  and  $D_p$  are the blank and punch diameters, respectively. When the discs have been manipulated into cups of a suitable size, these are then converted into tubes of smaller diameter and thinner wall by conventional draw-bench methods. The grain-size of the material for the cupping operations must be carefully controlled to avoid "orange-peel" effects.

In the draw-bench operations, single reductions of area up to 35% can be given, with total reductions of 60–80%, before annealing is necessary, the selection of the appropriate point for stress-relieving depending on the thickness : diameter ratio of the tube.

Niobium has a strong tendency to gall when being drawn into tubing and an effective lubricant must be used in order to prevent this occurring. In addition to this the types of material used for tools, i.e. dies and punches, also influence the drawing characteristics. Aluminium bronze, tungsten carbide, and hard chromium-plated tools have been used, aluminium bronze in the main being the most successful.

### 2. ROD AND WIRE

The production of rod and wire follows a similar sequence to that of strip production, except that in this case the starting point is normally square bar, and the rolling operations are replaced by swaging or rod rolling. Techniques for wire drawing have been developed, but difficulties are at present being met with in attempts to use conventional high-speed wire-drawing methods

particularly for fine wire, owing again to the "galling" of the wire on to the dies.

### 3. EXTRUSION

Little is so far known regarding the extrusion of niobium. The inherently good formability of the metal suggests, however, that suitable techniques could be developed, if the demand for such products arose.

## VII.—WELDING

The most important factors affecting the weldability of niobium are its high melting point and its reactivity at elevated temperatures. The basic requirements are thus a high rate of heat input and an inert atmosphere, and the choice of method is limited to resistance welding or modified argon-arc or helium-arc techniques.

Spot-welding methods have been successfully applied, and sound ductile joints produced. Modifications to the normal argon-arc technique are essential to ensure that the argon blanket covers the metal until it has cooled to less than, say, 200° C. This can be achieved by using a container which is purged by evacuation and subsequently filled with argon. Both A.C. and D.C. techniques are applicable, and bright silvery welds can be produced having a tensile strength approximately 85% of that of the parent metal.

## VIII.—CONCLUSIONS

The paper summarizes some of the more important aspects of the sintering and fabrication of niobium, using techniques based on the integration of high-vacuum technology with the arts of powder metallurgy. Considerable progress has been made in an understanding of the relative importance of the numerous variables involved, and the major problems associated with the establishment of an operational procedure have now been overcome. Much, however, still remains to be done. One of the next major steps will probably be to investigate the behaviour of alloys, and preliminary indications

are that important differences in technique may be required.

As the availability of the metal increases, alternative applications both within and outside the field of nuclear power may emerge, and it is possible that the next few years will see rapid advances in the metallurgy of this, the most recent addition to the group of metals required and used, even though on a small scale, as special-purpose materials.

## ACKNOWLEDGEMENTS

The work presented is based on the results of development work at the Springfields and Culcheth Laboratories of the Research and Development Sections of the United Kingdom Atomic Energy Authority (Industrial Group), and acknowledgement is made to colleagues whose work has been included, particularly as no open reference to individual papers has been possible, owing to their classified nature. The author also wishes to thank Mr. C. Cashmore, of Messrs. Accles and Pollock, Ltd., for information relating to tube-drawing techniques and to record his appreciation of discussions with Dr. G. L. Miller of Murex, Ltd.

Thanks are also due to Sir Christopher Hinton, K.B.E., F.R.S., Managing Director, and Mr. L. Rotherham, Director of Research and Development, of the United Kingdom Atomic Energy Authority (Industrial Group), for permission to publish the paper.

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RADIOGRAPHS ILLUSTRATING FORMS OF SHRINKAGE.  
(See text, p. 364)

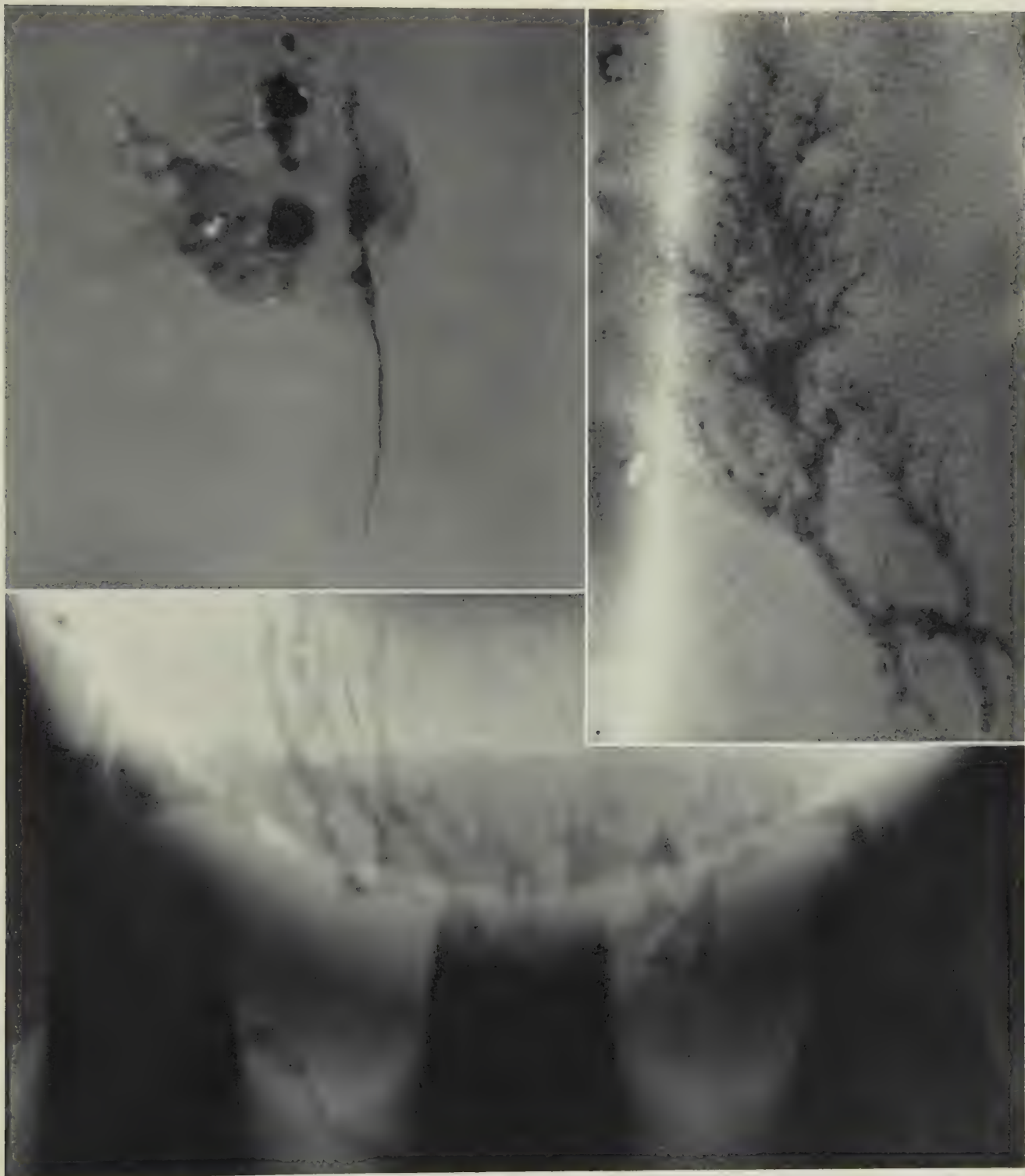
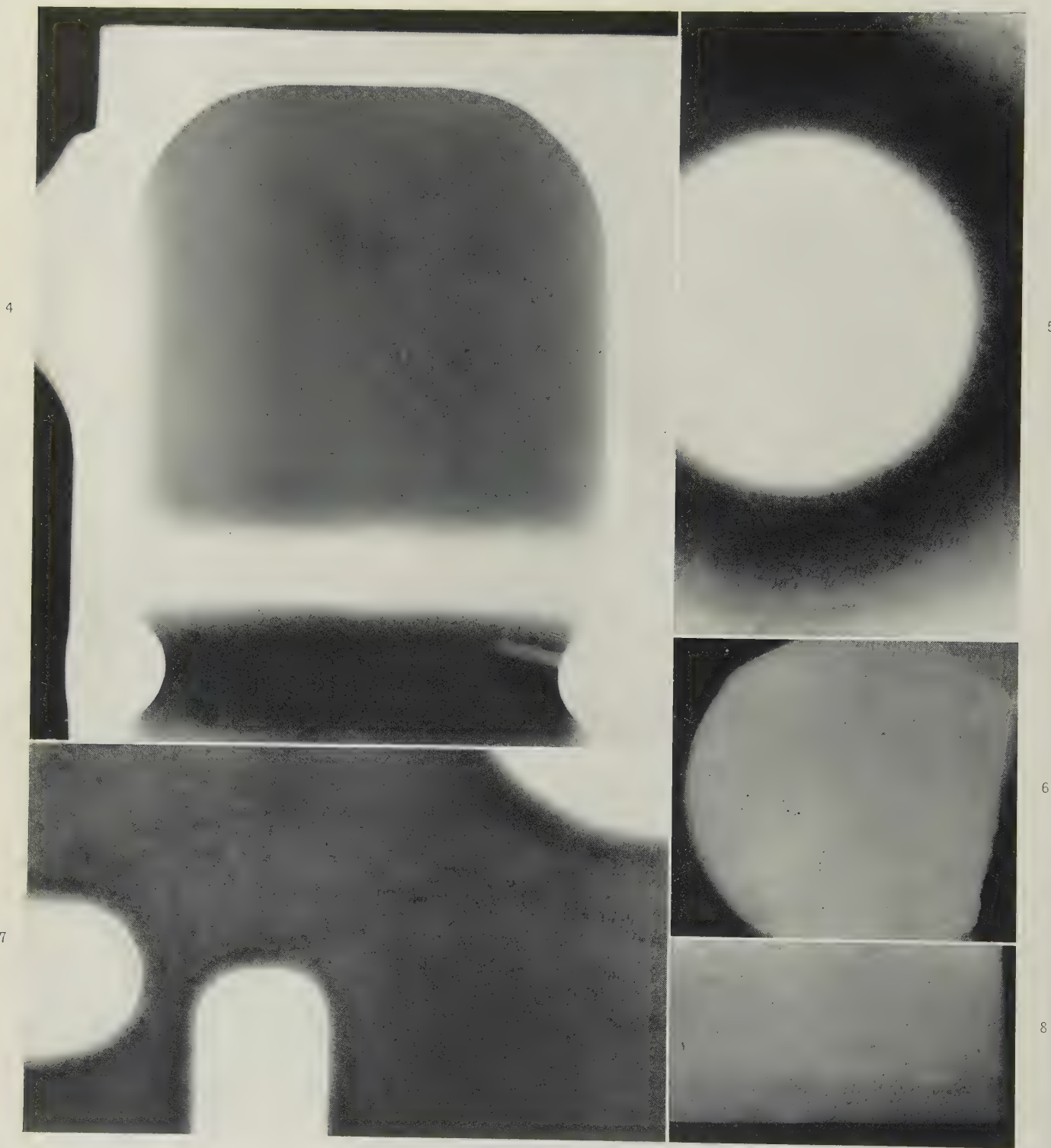


FIG. 1.—Magnesium-Zirconium Alloy D.T.D. 748.  
FIG. 2.—Aluminium-Silicon Alloy LM8.  
FIG. 3.—High-Conductivity Copper.

All taken using X-rays with the exception of Fig. 3, for which a cobalt <sup>60</sup> source was used. Figs. 1 and 3 on high-contrast film ; Fig. 2 on medium-contrast film.

RADIOGRAPHS ILLUSTRATING FORMS OF SHRINKAGE.  
(See text, p. 364)



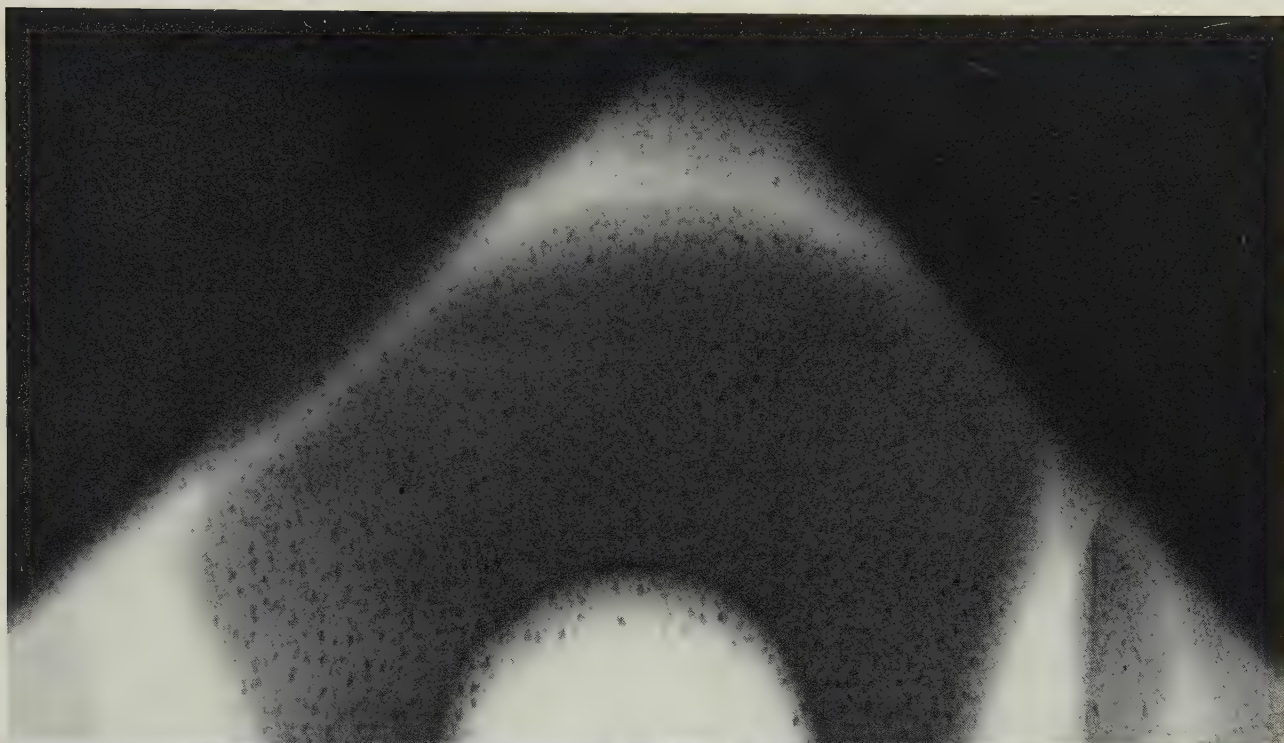
FIGS. 4-6.—Aluminium-Magnesium Alloy L53.  
FIG. 7.—Magnesium-Zirconium Alloy D.T.D. 748.  
FIG. 8.—Magnesium-Aluminium Alloy L124.

All taken on high-contrast film using X-rays.



## RADIOGRAPHS ILLUSTRATING GAS POROSITY IN ALUMINIUM ALLOYS.

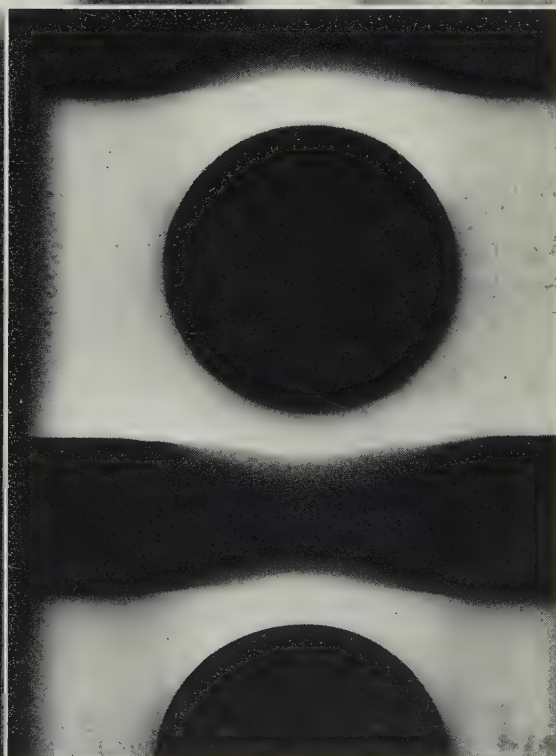
(See text, p. 364)



9



10



11

FIG. 9.—Aluminium-Silicon Alloy L33.  
FIG. 10.—Aluminium-Copper Alloy D.T.D. 304.  
FIG. 11.—Aluminium-Silicon Alloy D.T.D. 245.

All taken on medium-contrast film using X-rays.

RADIOGRAPHS ILLUSTRATING OXIDE INCLUSIONS AND BLOWS.  
(See text, p. 364)

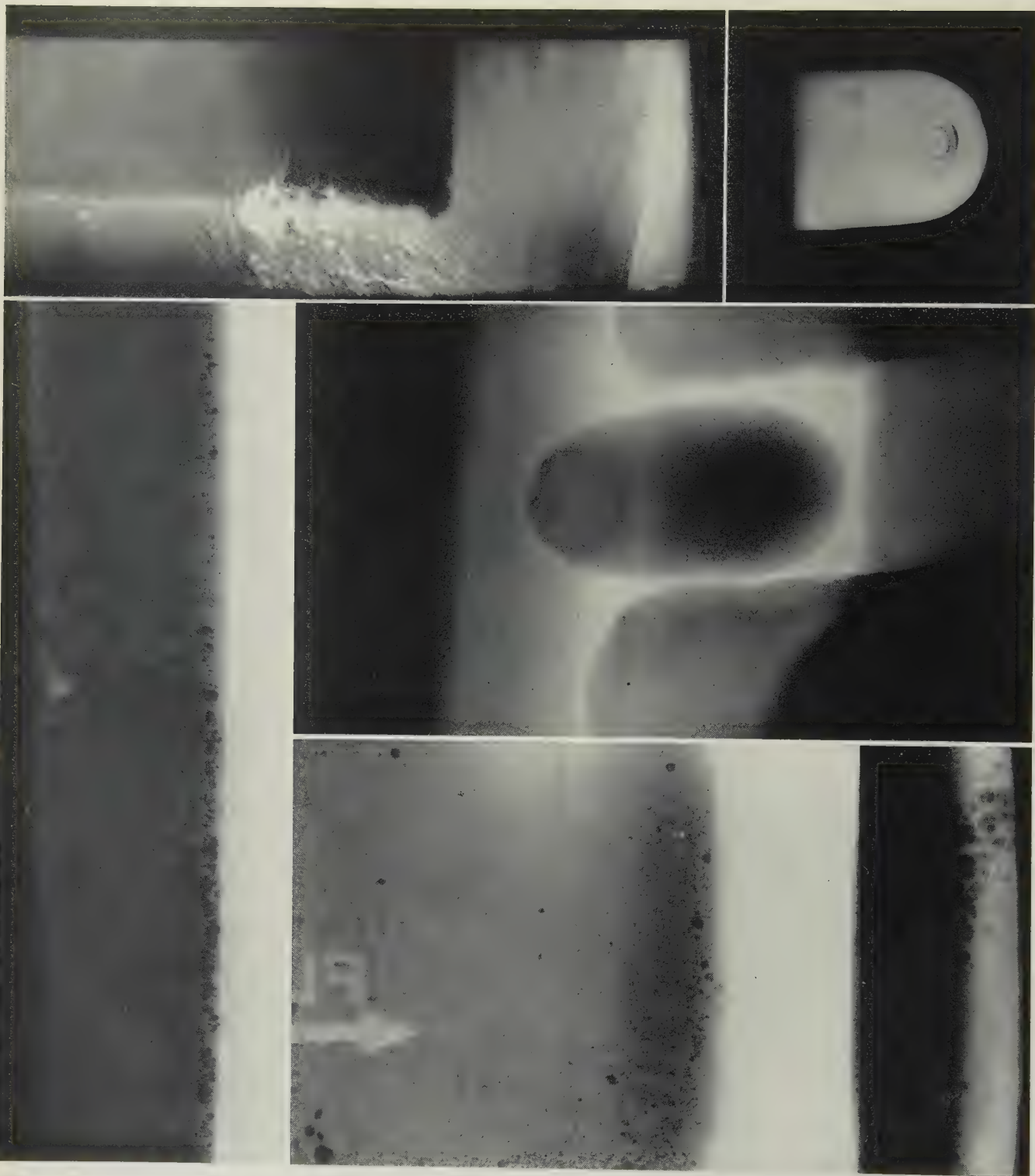
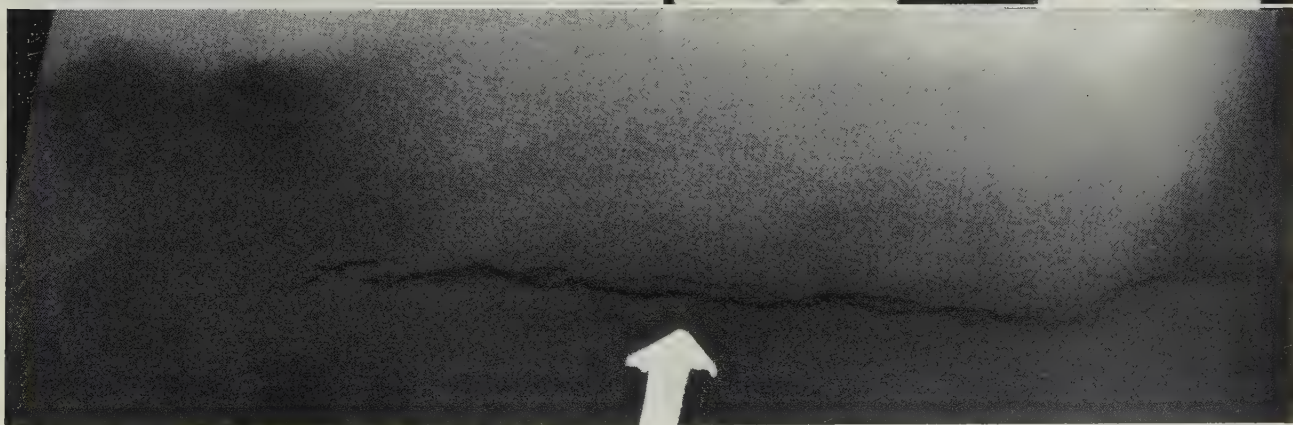
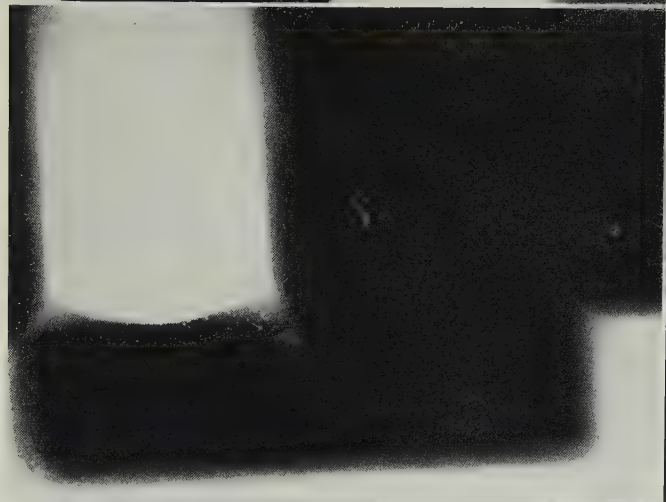


FIG. 12.—Magnesium-Thorium Alloy ZT1.  
FIGS. 13 and 16.—Magnesium-Aluminium Alloy L122.  
FIG. 14.—Aluminium-Copper-Silicon Alloy L51.  
FIG. 15.—Magnesium-Zirconium Alloy D.T.D. 748.

All taken using X-rays. FIGS. 12-13 and 15-16 on high-contrast film; FIG. 14 on medium-contrast film.



RADIOGRAPHS ILLUSTRATING CRACKS  
(See text, p. 365)



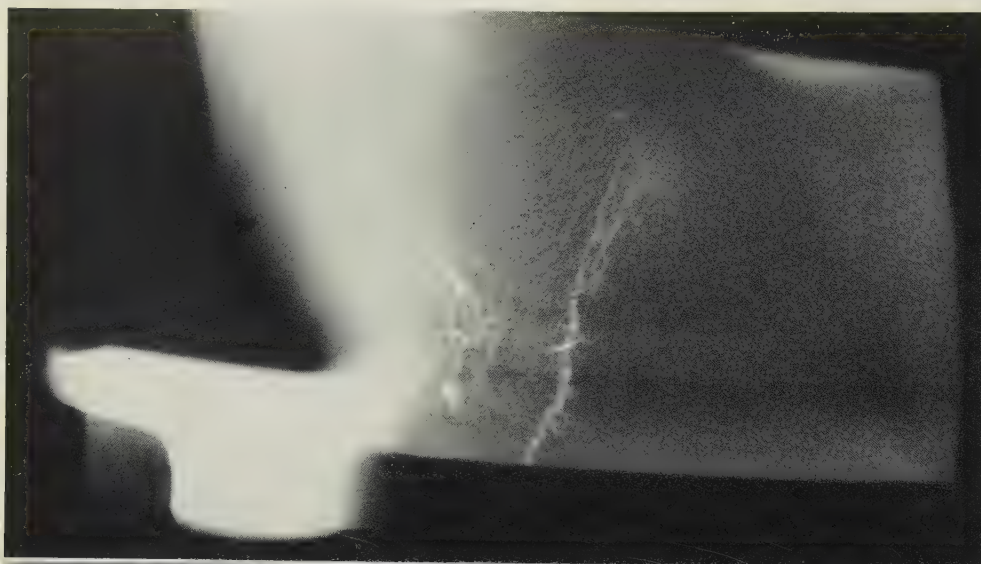
FIGS. 17 and 19.—Magnesium-Aluminium Alloy 1.122.  
FIG. 18.—Aluminium-Magnesium Alloy L53.  
FIG. 20.—Magnesium-Zirconium Alloy D.T.D. 748.

All taken on high-contrast film using X-rays.

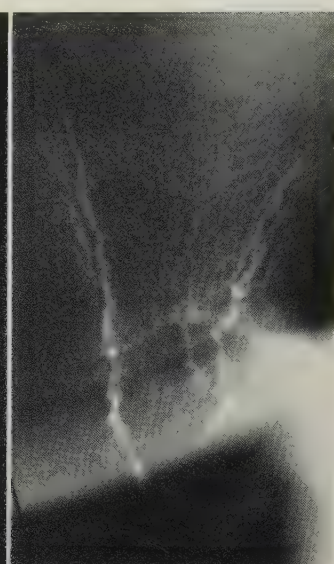


RADIOGRAPHS ILLUSTRATING SEALED SHRINKAGE OR TEARS.  
(See text, p. 365)

21



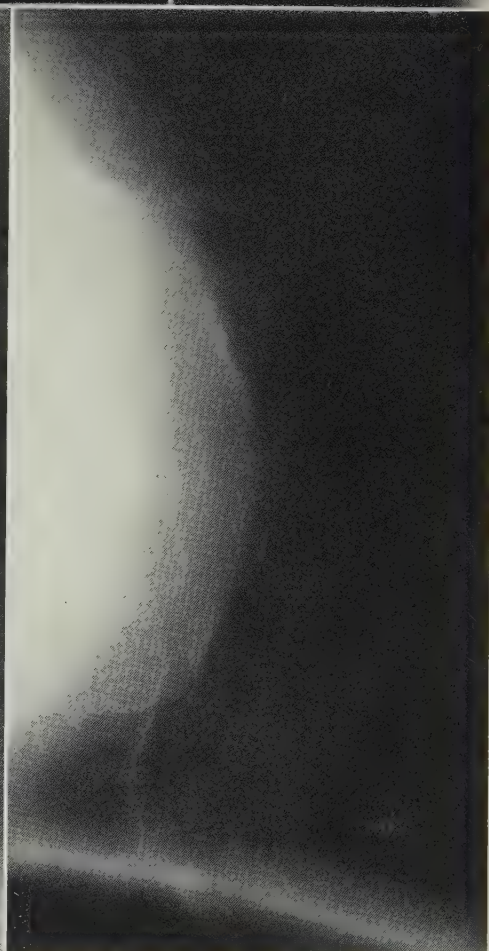
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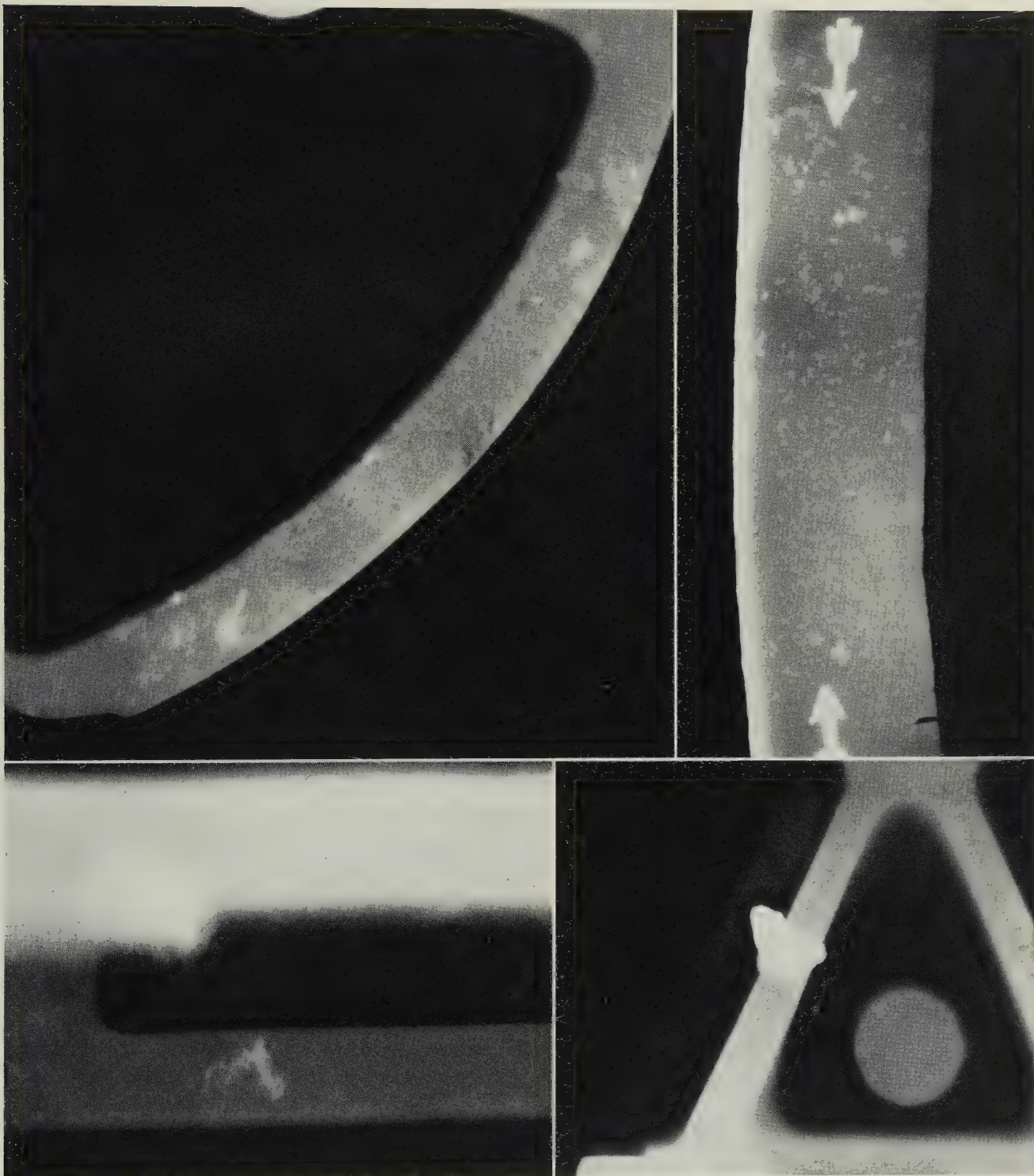


FIGS. 21 and 22.—Magnesium-Thorium Alloy ZT1.  
FIGS. 23 and 24.—Magnesium-Zirconium Alloy D.T.D. 748.

All taken on high-contrast film using X-rays.



RADIOGRAPHS ILLUSTRATING DENSE INCLUSIONS.  
(See text, p. 365)



26

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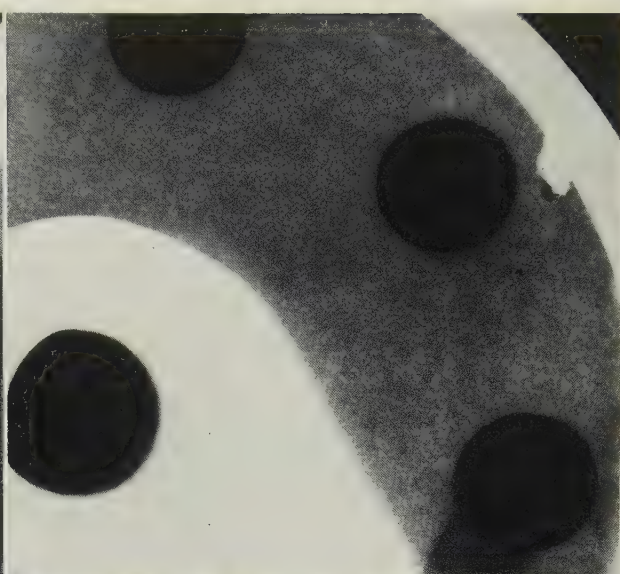
FIG. 25.—Magnesium-Aluminium Alloy L122.  
FIGS. 26 and 27.—Magnesium-Zirconium Alloy D.T.D. 748.  
FIG. 28.—Magnesium-Zirconium Alloy D.T.D. 721.

All taken on high-contrast film using X-rays.

## MISCELLANEOUS RADIOGRAPHS.

(See text, p. 365)

29



32



FIGS. 29 and 31.—Magnesium-Aluminium Alloy L122.

FIG. 30.—Magnesium-Zirconium Alloy D.T.D. 748.

All taken on high-contrast film using X-rays.

FIG. 32.—Enlarged Radiograph of Test-Piece for Assessing Resolution of X-Ray Film (see text, p. 366).  $\times 4$ .



## MICROSTRUCTURES OF NIOBIUM

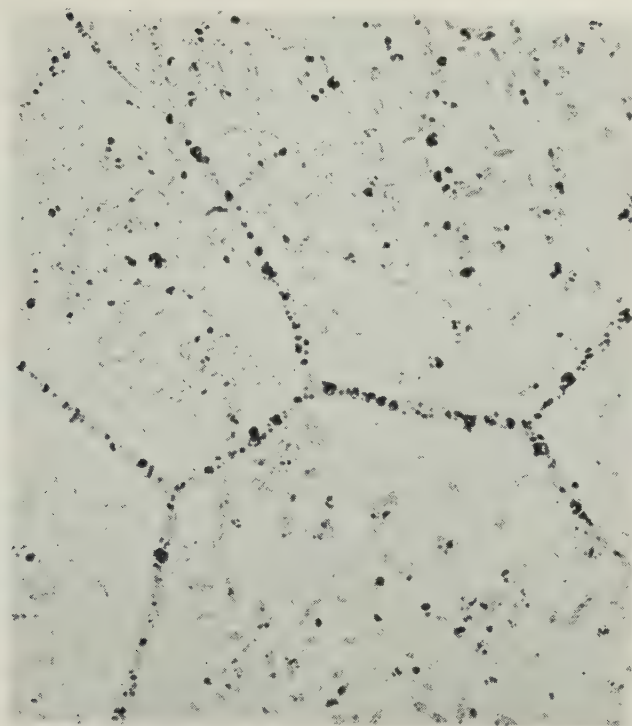


FIG. 4.—Transverse Section of Specimen 2. Unetched.  $\times 150$ .

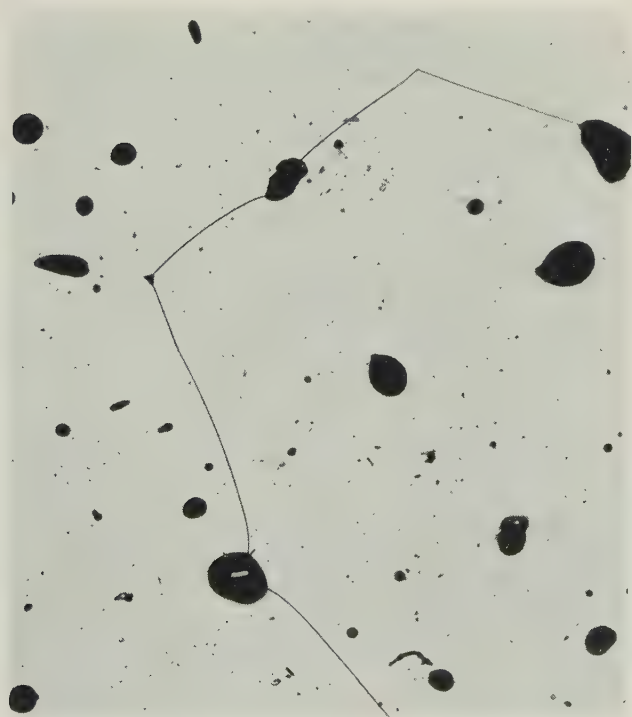


FIG. 5.—Transverse Section of Specimen 5. Etched in 95%  $\text{HNO}_3$  (conc.) and 5% HF (40%).  $\times 150$ .

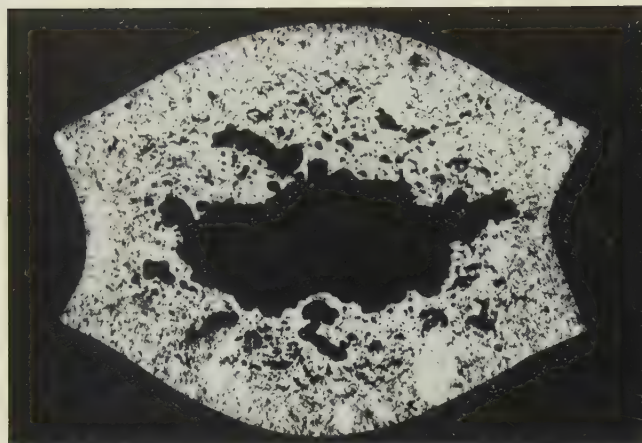


FIG. 2.—Cross-Section of Niobium Compact Rapidly Heated ( $30^{\circ}\text{C./min.}$ ) to  $2300^{\circ}\text{C.}$  and Sintered for 1 hr.  $\times 7\frac{1}{2}$ .



FIG. 3.—Cross-Section of Niobium Compact Slowly Heated ( $5^{\circ}\text{C./min.}$ ) to  $2300^{\circ}\text{C.}$  and Sintered for 3 hr.  $\times 7\frac{1}{2}$ .

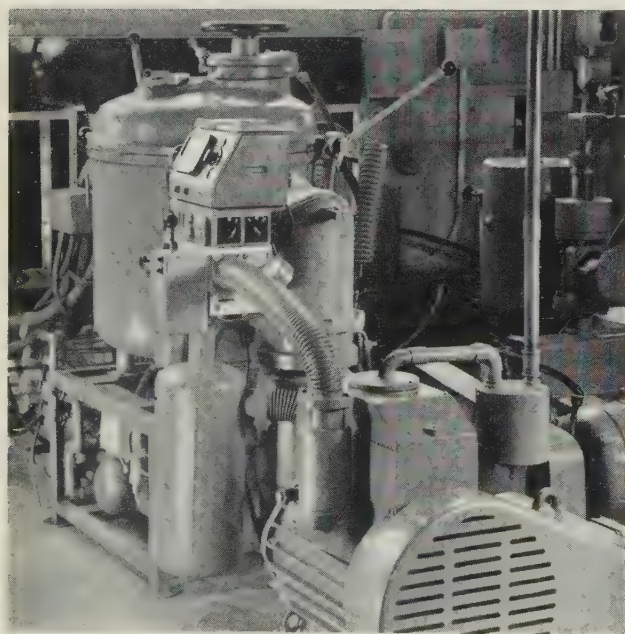


FIG. 4.—Furnace Unit.

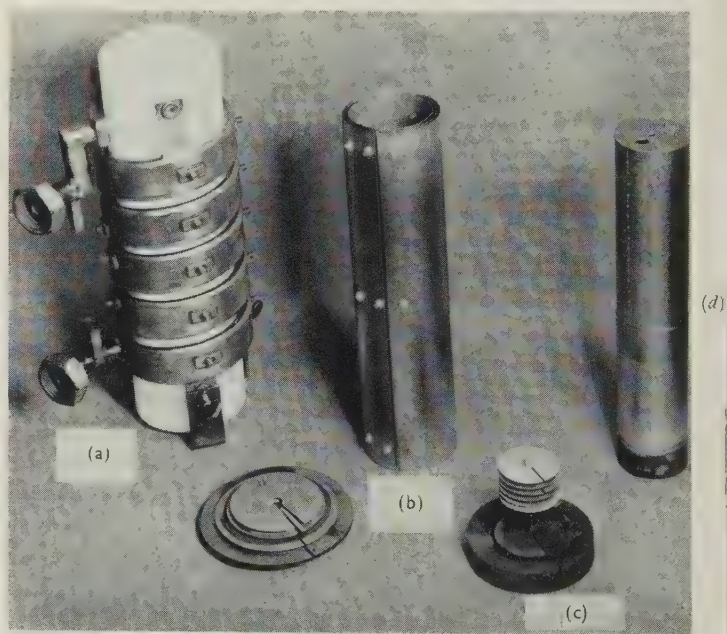


FIG. 5.—Sintering Apparatus. (a) H.F. coil and silica lining; (b) molybdenum radiation screens; (c) carbon support and lower screen; (d) tungsten susceptor and lid.





FIG. 7.—Sintered Niobium Sheet.  $\times 100$ .

FIG. 8.—Sintered Niobium Sheet after 25% Reduction of Area.  $\times 100$ .

FIG. 9.—Niobium in Sheet Form.  $\times 100$ .





# METALLURGICAL PROBLEMS OF ATOMIC ENERGY\* 1760

By L. ROTHERHAM,† M.Sc., MEMBER

## SYNOPSIS

A short account is given of metallurgical problems arising in connection with (a) structures, (b) fuels, and (c) special metals requirements.

## I.—INTRODUCTION

MANY papers have been presented in recent years on metallurgical problems arising in the new atomic-energy industry. These papers have tended to emphasize those metallurgical features which are unique to atomic energy rather than those problems which are, to some extent, common to atomic energy and other branches of engineering. A good example is the effect of irradiation on the properties of metals, a branch of metallurgy bordering closely on solid-state physics and one which would not be observed in other branches of engineering. It is natural that these very interesting phenomena should be the subject of considerable study and that many excellent scientific papers should therefore be forthcoming, but over-emphasis of these particular studies would give an unbalanced overall view of the metallurgical effort which has been made available to further the nuclear-energy programme. The majority of the problems met with in nuclear energy are not fundamentally different from those of any other engineering industry, although those of us working in the atomic-energy industry tend to think that perhaps we cover a wider range of problems. However, even this point of view is difficult to sustain when the range and interest of metallurgical development in fields such as the aircraft industry, gas turbines, many branches of structural engineering, and so on, are considered.

There is one important feature of atomic energy, however, which offers a particularly satisfying career to the metallurgist. It is a new industry, which is developing at a very rapid pace and in which large new projects are, from time to time, being begun. The position of the metallurgist in the industry is one of close association with the project engineers, and he must be a party to the decisions taken from the earliest planning stages. The level of responsibility of the metallurgist from the beginning to the end of a pioneering project is high, and this, to some extent, is unique in the industries of the country.

In what follows I shall attempt to present an overall picture of work in the atomic-energy field from a metallurgist's point of view, with a conscious effort to identify the problems which are dealt with and point to analogies with similar problems in other industries. The whole range of work is too great to be dealt with in the space of a short lecture, and I shall attempt to draw examples from the following fields only: (a) structures, (b) fuels, and (c) special metals requirements.

## II.—STRUCTURES

The most interesting cases of structural problems that arise in atomic-energy work are those of the large steel vessels required for a number of purposes. In this connection the problem of the metallurgist is primarily to advise on the selection of materials and to assist in defining satisfactory standards of supervision for fabrication and inspection of the vessels, especially during construction on the site of the project. The general experience with structures of this particular type is that, since failures cannot be tolerated, the design must be reasonably conservative. However, if this conservatism is carried to the point where only existing experience and practice can be used, then progress will be slow; in fact, we are always attempting to extrapolate from our existing experience to some more advanced technology.

As an example of the type of structure to be kept in mind when considering this class of problem, it is perhaps worth quoting the size of some of the steel vessels built in recent years. For example, the steel sphere for containing the Dounreay fast-fission reactor is 130 ft. in dia. and is constructed from a mild-steel plate about 1 in. thick. The size of this sphere is comparable with, although rather bigger than, the containing vessels required for experimental reactors such as the DIDO reactor at Harwell or the similar D.M.T.R. experimental reactor at Dounreay. The pressure vessels which contain the nuclear core of the Calder Hall reactors are approximately 40 ft. in dia. and 70 ft. long. These were welded up from 2-in. plate, but with plate thicknesses up to 4 in. at the points of entry of the gas ducting. The gas ducts themselves, of course, are of steel construction and connect with other large steel vessels in which the hot gas exchanges its heat with water and steam to give the working fluid for the steam turbines. It is interesting to remember that all these vessels are too large for works assembly and must be built up near to the point where they are to be used. Dangers may arise from the effects of damp and cold during the construction period. Damp welding electrodes, with the consequent possibilities of hydrogen in the weld metal, may give inferior properties, and cold weather increases the possibility of brittle failures of these very large structures. It is difficult to assess the importance of a low temperature for the transition from ductile to brittle fracture in steels, since it is not a characteristic which can be readily introduced as a design parameter, but everyone would

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probably agree that, all other things being equal, a low temperature of transition would be regarded as desirable. The facts available on the conditions under which brittle fractures can occur are, on the whole, not in favour of the requirements for nuclear-energy purposes. For instance, the vessels used at Calder Hall were the largest vessels in the plate thickness adopted which had been made in this country up to the time of their construction, and it is known that brittle failures are more common in large vessels and in thick plates than in small vessels and thin plates. Furthermore, the effect of irradiation is to raise the temperature of transition from ductile to brittle failure. This again is an undesirable characteristic. Moreover, the service conditions of the Calder Hall reactors are such that the incidence of high-temperature creep is on the verge of being a limiting factor also. It is well known, of course, that a good notch-tough steel can be produced by suitable deoxidation practice. Unfortunately, the methods used to give good notch ductility in general tend to result in a reduction in the creep strength of the steel; the problem here is, therefore, in part one of engineering design to ensure the best possible service conditions so that available steels may be used with proper regard to creep and brittle fracture. In part, however, the problem which we shall face more particularly in the future, as service temperatures increase, will be the development of steels which combine high notch-toughness with high creep strengths and attractive welding properties for the construction of vessels under difficult site conditions.

One further point in relation to pressure vessels is perhaps worth mentioning. With a large structure it is well known that the incidence of brittle fracture may be dependent on the existence of stress-concentration factors and internal stresses within the structure. It is virtually impossible to eliminate all notches or other stress-raisers, but it is possible, in most cases, to reduce their effect by eliminating or reducing internal stresses by a stress-relieving treatment. In the case of the Calder Hall reactor pressure vessel, it was decided that it would be desirable to stress-relieve the very large vessels after construction and installation within their concrete housing, and this was successfully accomplished by building, within the reactors, an electric-heating grid through which a heavy current could be passed. The pressure vessels themselves were, of course, lagged, as they must be lagged in service to retain heat, and were then gradually raised to a satisfactory relieving temperature. After reaching an adequate maximum temperature, the vessels were allowed to cool slowly to room temperature, and during both heating and cooling operations careful records were taken of the temperature distribution throughout the vessels and the strains resulting from the heating and cooling operations. It is not possible, of course, to ensure an absolutely uniform temperature distribution throughout a vessel of the size involved here, but it is possible by careful observation to ensure that the lowest temperatures reached are sufficient to give adequate stress-relief, while the maximum temperatures are not so high as to exceed the critical point.

The construction of large vessels in the field and the control of fabrication, inspection, and heat-treatment is a most interesting practical problem, which will have to be faced for some years to come while large vessels of this type are used in nuclear engineering. This is, however,

only to be regarded as an example of the type of problem encountered in the constructional stages of nuclear-power development. Almost as interesting is the construction of chemical plants, such as those at Windscale, in which large quantities of stainless steel are used to process and store highly corrosive fission products under conditions where future examination of the plant is not likely ever to be possible. Special care must again be exercised to ensure absolute reliability in the plant. Similarly, the corrosion problems encountered in the use of uranium hexafluoride, the vapour of which is used in the gaseous diffusion plant at Capenhurst, introduces interesting corrosion problems. All these require intensive study to assist in the selection of materials and, once a material has been selected, new problems, such as the development of adequate welding techniques and the like, present themselves.

### III.—FUELS

The principal fuels used in nuclear reactors at the present time are based on natural uranium. Thorium and plutonium will undoubtedly have a place in future years, and already some enriched uranium is available for special purposes. The metallurgy of enriched uranium is, of course, the same as the metallurgy of natural uranium, and this has been studied thoroughly over the years, but only a little is known of the possible future fuels thorium and plutonium. The production of uranium metal has been described in other papers, but it may be briefly mentioned that bulk metal is readily produced by the reduction of uranium tetrafluoride with calcium or magnesium. The billet produced by such a reduction process is satisfactory either for casting into finished bars or for the manufacture of rolling billets for future working. Most of the possible manufacturing techniques, such as casting, rolling, and extrusion, have been studied, and it is interesting to note that the behaviour of the uranium in service may very well depend on the method adopted for its manufacture.

Irradiation damage can take one of two forms. For example, at long irradiation times a great deal of fission-product formation will lead to distortion and to swelling, particularly at high temperatures, but at low temperatures and at rather lower irradiation levels a different type of distortion may occur. In effect, and speaking qualitatively, it can be said that this low-temperature distortion is associated with the twinning deformation of uranium and what are effectively thermal stresses resulting from the passage of fission fragments through the lattice. It is a property of the single crystal of uranium and leads to growth in certain crystallographic directions and to contraction in others. It is, therefore, closely associated with the microstructure of the uranium fuel when we are considering the normal use of uranium in the form of uranium metal bars or components. Naturally, the microstructure depends on the methods of fabrication, and it can also be influenced by heat-treatment. The demonstration of the relationship between microstructure and irradiation damage is achieved by the metallographic examination of fuel which has been in service in Windscale and Calder Hall reactors and is readily observed, although the cost of examination of highly radioactive specimens may be considerable. A typical form of irradiation damage is a wrinkling of the surface of bars, and this is associated with a large grain-



size. It can, therefore, be eliminated or lessened by heat-treatment which reduces the grain-size. A satisfactory heat-treatment such as quenching from the  $\beta$  phase was developed, and an extensive study of transformation characteristics has been made.

There are some resemblances between the  $\beta \rightarrow \alpha$  transformation in uranium and the transformation from austenite to ferrite or martensite in the case of steel. At high temperatures the transformation is by nucleation and growth, whereas at low temperatures the transformation is by a shear mechanism. In both cases the addition of alloying elements will lead to a delay in the beginning of the transformation. It is, therefore, possible to study the effects of heat-treatment in uranium by many of the techniques used so successfully in the past with steels. For example, a good deal of work has been done on the heat-treatment of uranium and on the effects of alloying additions on the results by the technique of isothermal transformation at different temperatures and the construction of the so-called "time/temperature/transformation" ( $T/T/T$ ) curves, and this work is still continuing.

Another point which should be borne in mind when considering the performance of uranium in a nuclear reactor is that at the very minimum the uranium generally has to support its own weight. In some cases it has to act as a structural material, and indeed in the Calder Hall reactors the fuel elements are stacked one upon another in the vertical channels so that the bottom fuel element must support the whole length of the column, and to this extent it can be regarded as a structural material. It must, therefore, have an adequate resistance to deformation under the stress/temperature conditions prevailing in the reactor. Not a great deal of work has been done in the past on the high-temperature strength of uranium, but enough was carried out in the early days of the design of the Calder Hall reactors to reassure us that the strength would be adequate for this type of structure. However, since we can predict that the effect of development of reactor technology will be to lead to higher temperatures of operation, we obviously would wish to know how the creep strength of uranium can be increased. Again, the effects of alloying and heat-treatment on the high-temperature strength are studied. Indeed, when one considers the present position of the metallurgy of uranium as a fuel for reactors, it is obvious that a tremendous amount of further work remains to be done. We have reached the point where almost pure uranium can be used satisfactorily in nuclear reactors, but as service conditions become more and more onerous we quite clearly shall need to have information on a wide range of uranium alloys, both from the point of improving their resistance to deformation at high temperatures and their resistance to irradiation damage, although this latter may mean mainly the development of alloys of more adequate mechanical properties and heat-treatment response. The analogy with the development of alloy steels which has taken place over the last fifty years is obvious, and many of the same techniques and ideas will almost certainly be applicable.

#### IV.—SPECIAL METALS

In service the uranium metal fuel is enclosed in a protective container, which in the case of the Windscale

piles was made of aluminium and which in the Calder Hall reactors is of magnesium. It is perhaps undesirable to regard aluminium and magnesium as special metals, although the properties required in these applications are, in fact, quite special and different from those needed in ordinary commercial applications. The future reactors will probably require less-common metals, such as zirconium, beryllium, vanadium, or niobium, or even possibly molybdenum and tungsten, to be substituted for the present-day aluminium and magnesium, and these can quite properly be regarded as special metals. The service conditions will be such that the containers will certainly be subjected to a high neutron flux, probably with a high temperature and usually with high stresses and corrosive environments, either of liquid or gases.

To indicate the trend of development, it is perhaps easiest to consider the case of the Calder Hall reactors, where, as already indicated, magnesium is used as the envelope for the uranium. Magnesium appears to be an excellent material for this application, provided that the temperature is not too high, but even for service at temperatures as high as 400°–500° C. it was necessary to develop alloys with additional oxidation-resistance to reassure the designers that magnesium would be safe. An alloy satisfactory from this point of view having been produced, the manufacturing process for the so-called "Magnox" alloys is by casting, extrusion, and machining of a finned container into which the uranium bar fits. This is then sealed by end-welding with automatic welding equipment. The resulting product appears to be satisfactory, but the process of development has required studies at almost every point in the manufacturing process. For example, even at the casting stage, slag inclusions and other non-metallic matter proved difficult to eliminate. Extrusion difficulties were encountered, and the alloy originally chosen was found to be extremely difficult to weld. The latter point was dealt with by a change in composition, but the alloy, which contains beryllium, was still found to be prone to an excessive grain growth. Changes in composition were once again necessary. Even when all these difficult problems had been eliminated, it was still known that magnesium as a metal is rather prone to the formation of cavities between the crystal grains under deformation both at a low and a high temperature and that under some conditions of deformation under creep conditions it has a low ductility. Again a systematic study, largely empirical in nature, had to be undertaken to minimize these effects. It would be rash to claim that all the problems in the use of magnesium as a cladding material in reactors have been solved, but it does appear that, as a result of the very intensive work which was carried on, the material will prove to be satisfactory.

There can be little doubt, however, that the future of nuclear energy will require the use of higher temperatures than have so far been called for, and magnesium has the unattractive features of a low melting point and a high volatility even below the melting point; these two features are likely to preclude its use at temperatures very much in excess of those being used at present, and for advanced thermal reactors, therefore, we shall certainly have to select other materials. Of the materials available, only zirconium and beryllium have both a high melting point and a low absorption cross-section for thermal neutrons, and it is likely, therefore, that one or

other of these two elements will be used in future reactors of the Calder Hall basic type. Beryllium is especially attractive in that it has a lower absorption cross-section than magnesium or aluminium and has much better high-temperature properties. It is also compatible with the likely heat-transfer fluids such as carbon dioxide, hydrogen, or certain liquid metals. On the other hand, it has been made only in small quantities hitherto, and it is known to exhibit very low transverse ductility in certain circumstances. The work in this country in the past has largely been carried out at the Atomic Energy Research Establishment, Harwell, and at the Atomic Weapons Research Establishment, Aldermaston, and has consisted of work on the formation of reactor components by straightforward forming operations. This is not expected to present a great deal of difficulty, but the canning of uranium in beryllium may prove more difficult. Work on conventional canning methods, i.e. tube production followed by the insertion of fuel and the welding-on of ends, is difficult because of the low transverse ductility, which may not accommodate growth of the fuel, and in addition the weld may prove brittle. Alternative methods, therefore, such as the co-extrusion of uranium with beryllium have been attempted, and these appear to be promising. Tests of fuel elements manufactured in this and other ways indicate that a satisfactory service life can be achieved. However, it is one thing to be able to make one or two sample specimens for laboratory investigation and another to make the same type of specimen by industrial processes and in lots of thousands or more. At the present time, the development of the processes to an industrial scale has still to be attempted. We feel, however, that the feasibility of using beryllium is now established and that the work remaining to be done lies in the development category.

If, however, the development of satisfactory processes for beryllium should prove too difficult, then zirconium would be a possible substitute. The technology of zirconium is rather more advanced than that of beryllium, and the metal has been produced in great quantities. The amount of development work that would be necessary, therefore, to bring zirconium into service in reactors would be less, and it is probable that this could be carried out in one or two years' time. There is little doubt that the high-temperature strength of zirconium will be increased, so that it could be used for structural members within a reactor; the main doubt in this case, however, is its resistance to attack by air and by carbon dioxide,

which are possible reactor coolants, and this may lead to some restriction on its use at the very highest temperatures. Zirconium, however, has a further possible use, both in sodium-cooled reactors and in water-cooled reactors; especially in the latter case, its very high resistance to attack by hot water leads to the indication that this is probably its most suitable application.

In this country the use of the other metals I have mentioned—niobium, vanadium, molybdenum, tungsten, &c.—is primarily in liquid-metal-cooled reactors. In the case of all these materials one of the most most interesting features from a metallurgical point of view is that the new metals often require new metallurgical techniques. In our own laboratories we have used sintering and melting methods in which a higher vacuum has been obtained than is customary in vacuum metallurgical operations. This has been achieved by providing very large vacuum pumps, and the high pumping speeds then possible can give excellent purification of the metal from impurities such as oxygen, hydrogen, and nitrogen. Experience has been acquired so that it is now possible to design in detail the equipment for specific applications. Much of this work will be published in the near future, and it is hoped that it will prove of value to others who may be entering this field of vacuum metallurgy.

The purification achieved by vacuum techniques is important in that it gives a metal of adequate quality for fabrication by established techniques, for instance, tube manufacture by cupping and drawing. The development of the newer metals is essentially one of introducing new processes at some critical point in a chain of operations that has been established for more conventional metals. To this extent it is raising our technological standards generally.

## V.—CONCLUSIONS

This brief review has, I hope, shown that metallurgical work in atomic energy embraces a wide range of problems. These include problems ranging from large structural materials down to small components, and in metals as familiar as mild steel or aluminium, or as new as plutonium or niobium and beryllium. In many cases solutions can be found by techniques which have been well tried in the past, but, in other cases, it may be necessary to consider the development of new methods. This broad sweep of metallurgical problems probably forms the most fascinating feature of metallurgy in the atomic-energy industry.



# THE EFFECT OF NEUTRON IRRADIATION ON THE MECHANICAL PROPERTIES OF TITANIUM AND ZIRCONIUM \*

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By M. J. MAKIN,† B.Sc., Ph.D., and F. J. MINTER†

## SYNOPSIS

The changes in mechanical properties of titanium and zirconium after irradiation with  $5 \times 10^{19}$  neutrons/cm.<sup>2</sup> have been studied at a variety of temperatures.

The yield stress of annealed titanium increased by about 8000 lb./in.<sup>2</sup> at all testing temperatures between  $-195^{\circ}$  and  $+200^{\circ}$  C. A yield point was developed at  $200^{\circ}$  C., which indicates the migration to dislocations of vacancies produced by the irradiation. The elongation before fracture was reduced by the irradiation at all testing temperatures and the ultimate tensile strength increased slightly. The yield stress of heavily cold-worked zirconium decreased slightly at all testing temperatures after irradiation and the ultimate tensile strength rose. The elongation before fracture also increased, in marked contrast to the behaviour of annealed material.

The reason for this "annealing" effect in heavily cold-worked metal is discussed in terms of the atomic defects produced and also in terms of the Brinkman displacement-spike mechanism.

## I.—INTRODUCTION

THERE are numerous papers in the literature which report that the resistance of metals to deformation is markedly increased by irradiation with fast particles. Sutton and Leiser<sup>1</sup> and Leiser<sup>2</sup> have reported the effect of neutron irradiation on a wide variety of engineering materials, including many plain carbon and stainless steels. The results indicate that softer materials show greater hardening on irradiation than harder materials, and that the effects tend to saturate at high doses. The elongation before fracture was reduced 20–30% by irradiation. The ductile  $\rightarrow$  brittle transition temperature of boiler steels was raised by irradiation, the increase depending upon the type of steel.

The behaviour of molybdenum under neutron irradiation has been studied by Bruch, McHugh, and Hockenbury.<sup>3</sup> Doses of between 1.9 and  $5.9 \times 10^{20}$  neutrons/cm.<sup>2</sup> raised the ductile  $\rightarrow$  brittle transition temperature from  $-30^{\circ}$  to  $+70^{\circ}$  C. and hence the material was completely brittle at room temperature after irradiation. Bruch *et al.* showed that although both the flow-stress/temperature curve and the fracture-stress/temperature curve were raised, the former was raised much further than the latter, thus causing the rise in transition temperature.

Konobeevsky, Pravdyuk, and Kutaitsev<sup>4</sup> have reported Russian work on the effect of neutron bombardment on the hardness, tensile strength, and microstructure of a number of metals. Zirconium became heavily twinned and partially recrystallized during the irradiation, which was carried out at between  $250^{\circ}$  and  $300^{\circ}$  C. Unfortunately, control specimens were not used, so that it is not certain whether these effects were genuinely due to irradiation or to long soaking at the irradiation temperature.

The changes in mechanical properties of zirconium after neutron irradiation have been investigated by Kemper and Kelly<sup>5</sup> who irradiated both annealed and work-hardened specimens to various neutron doses up to  $2.4 \times 10^{20}$  slow neutrons/cm.<sup>2</sup> They found that the increase in yield stress produced by the irradiation was greatest in the annealed material and became progressively less with increasing amounts of cold work. The increase in ultimate tensile strength and decrease in ductility on irradiation were not so much affected by previous cold work. Saturation of the irradiation effects occurred at about  $5 \times 10^{19}$  neutrons/cm.<sup>2</sup> Recovery of the irradiation damage was observed at a lower temperature than recovery of cold work; 40% recovery occurred in 100 hr. at  $300^{\circ}$  C.

The present paper describes the results of some neutron-irradiation experiments on titanium and zirconium, in which the effect of the testing temperature and of previous heavy cold work were investigated.

## II.—EXPERIMENTAL PROCEDURE

Materials of normal commercial purity were used so that the results might be applicable to reactor technology. The titanium was supplied by Imperial Chemical Industries, Ltd., and the zirconium by Murex, Ltd. The results of spectrographic analyses are given in Table I.

All the specimens were wires 6 in. long  $\times$  0.040 in. in dia. The use of wires reduced the radioactivity of the irradiated samples and ensured that a large number of specimens could be given an equal irradiation dose. They were prepared by the manufacturer by drawing down from  $\frac{1}{4}$ -in. rod. The titanium specimens were annealed at  $850^{\circ}$  C. for 24 hr. before irradiation. The

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zirconium specimens were not annealed and were irradiated in the hard-drawn condition.

Metallographic examination was carried out before irradiation. Several titanium specimens were polished mechanically, followed by attack polishing with a suspension of  $\gamma$ -alumina in 3% oxalic acid solution. To determine the grain-size, the specimen was lightly etched in a mixture of HF and HNO<sub>3</sub> in glycerine and photographed under polarized light. A fine and uniform grain structure was revealed, with an average grain dia. of 0.030–0.040 mm. The non-metallic inclusions in the zirconium were examined after polishing with dia-

measured to within 0.1% of the maximum value. The strain was measured directly from the motion of the cross-head to an accuracy of 0.01%. A strain rate of  $8.2 \times 10^{-5}$ /sec. was used in all the experiments. Tests at various temperatures were performed by surrounding the specimen with either a liquid bath or a furnace in which temperatures up to 400° C. were attainable.

TABLE I.—*Impurity Content of Titanium and Zirconium.*

Impurity	% in Titanium *	% in Zirconium †
Iron . . . . .	0.05	0.02
Copper . . . . .	0.005	0.005
Tin . . . . .	0.01	Not detected
Nickel . . . . .	Not detected	0.005
Aluminium . . . . .	0.001	Not detected
Calcium . . . . .	0.001	0.001
Magnesium . . . . .	0.001	0.0001
Bismuth . . . . .	Not detected	...
Silicon . . . . .	0.001	0.001
Manganese . . . . .	0.001	0.0005
Titanium . . . . .	...	0.001
Chromium . . . . .	Not detected	0.001
Hafnium . . . . .	...	Present
Sodium . . . . .	0.005	Not detected

\* None of the following elements was detected in titanium: niobium, tantalum, silver, lead, cobalt, zinc, cadmium.

† None of the following elements was detected in zirconium: gold, silver, lead, cobalt, zinc, cadmium.

mond dust and light etching in a 10% solution of ammonium bifluoride. Owing to the heavily cold-worked state of the zirconium, no determination of the grain-size was possible.

The specimens were irradiated for 6 months in a Windscale pile at approximately 100° C.\* in a flux of  $6 \times 10^{12}$  slow neutrons/cm.<sup>2</sup>/sec. The total dose of slow neutrons was  $5.1 \times 10^{19}$  neutrons/cm.<sup>2</sup> The fast flux is not accurately known, but is estimated to be approximately equal to the slow flux in the positions used. To prevent damage during handling and transport, the specimens were mounted in batches of 24 in a robust aluminium jig in the form of a squirrel cage. The jigs were sealed in an argon atmosphere to prevent contamination during the irradiation. In all cases an equal number of control specimens were prepared and stored at the same temperature for the same time as the irradiation specimens. In this way spurious effects due to the thermal history of the specimens were eliminated.

Tensile tests on the specimens were carried out in a modified Hounsfield Tensometer, fitted with a motor drive. The general arrangement of the apparatus is shown in Fig. 1. The machine was mounted vertically and fitted with lead screens to protect the operators from the radiation from the specimen. The load was determined by the bending of a spring-steel beam, measured by the rotation of two mirrors attached to levers supported between the beam and the machine. With this device, the load on the specimen could be

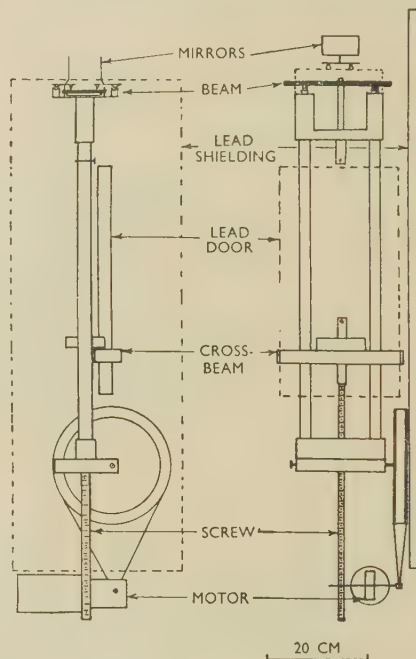


FIG. 1.—Tensile Testing Machine.

The results are presented both as normal stress/strain curves and as true-stress/true-strain curves in which the change in shape of the specimen during the extension is allowed for in the results. These latter curves represent the actual behaviour of the material more accurately than the conventional stress/strain curves.

The true stress and true strain are computed from the observed load and extension by the relations:

$$\text{true stress } \sigma' = \frac{L}{A_0} \cdot \frac{l}{l_0}$$

$$\text{true strain } \delta = \ln \frac{l}{l_0}$$

where  $L$  = load in kg.,  $A_0$  = initial cross-sectional area of specimen in mm.<sup>2</sup>,  $l$  = length of specimen, and  $l_0$  = initial length of specimen.

The term "yield stress" is defined as the stress required to produce 0.2% permanent deformation in the specimen.

### III.—EXPERIMENTAL RESULTS

#### 1. TITANIUM

The effect of irradiation on the tensile properties of titanium was investigated over a wide temperature range to establish the general pattern of behaviour. Four

\* The temperature of irradiation was not controlled, and varied between 80° and 110° C., at most.



specimens of the irradiated and four of unirradiated metal were tested at each of the following temperatures:  $-195^{\circ}$ ,  $-78^{\circ}$ ,  $20^{\circ}$ , and  $200^{\circ}$  C.

At  $-195^{\circ}$  C. the elongation before fracture of both the irradiated and unirradiated specimens was very low, and in some specimens it was zero. The irradiated material, however, consistently fractured at a stress about 10% greater than the unirradiated (Table II).

TABLE II.—*Tensile Tests on Titanium.*

(Limits of experimental results with the average values in parentheses.)

Temperature of Test, $^{\circ}$ C.	Unirradiated or Irradiated	Yield Stress, lb./in. <sup>2</sup> $\times 10^3$	Ultimate Tensile Strength, lb./in. <sup>2</sup> $\times 10^3$	$n$	Elongation, %
$-195^{\circ}$	Unirradiated	...	150.8	...	...
	Irradiated	...	145.4	...	...
$-78^{\circ}$	Unirradiated	95.5-105.5 (100.5)	101.5-119.6 (107.0)	0.12	10.0-11.2 (10.6)
	Irradiated	104.5-112.5 (108.5)	108.6-115.6 (112.1)	...	2.7-6.9 (4.8)
$20^{\circ}$	Unirradiated	78.0-81.6 (79.8)	79.9-86.9 (83.4)	0.08	9.0-11.8 (10.4)
	Irradiated	87.0-90.4 (88.7)	91.4-93.0 (92.2)	0.05	7.1-9.4 (8.3)
$200^{\circ}$	Unirradiated	36.4-38.0 (37.2)	51.6-54.6 (53.1)	0.12	8.2-10.6 (9.4)
	Irradiated	44.8-47.6 (46.2)	54.7-55.7 (55.2)	0.08	7.9-8.9 (8.4)

At  $-78^{\circ}$  C. both the irradiated and unirradiated specimens were ductile; the results are shown in Table II and in Fig. 2, where the mean curves and the limits of scatter are plotted. Both the yield stress and ultimate

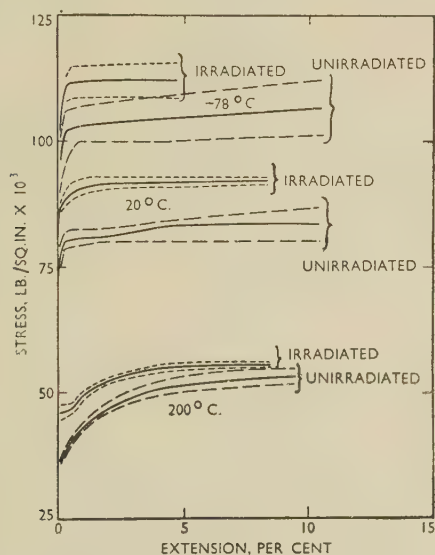


FIG. 2.—Average Stress/Strain Curves for Titanium at Various Testing Temperatures, with Limits of Scatter.

tensile strength were raised by the irradiation, and the elongation before fracture was reduced by about 50%. The effect of the irradiation is apparent throughout the stress/strain curve, and the increase in ultimate tensile strength was only slightly less than the increase in yield stress. No evidence of a true yield point, either before or after irradiation, was detected. True-stress/true-strain curves (Fig. 3), calculated from the mean curves in Fig. 2, indicate that the increase in flow stress produced by the irradiation decreases with increasing

extension, i.e. the rate of work-hardening has been reduced.

At  $20^{\circ}$  C. the yield stress of both the irradiated and unirradiated specimens (Fig. 2) was considerably lower than at  $-78^{\circ}$  C., but the increase in stress due to

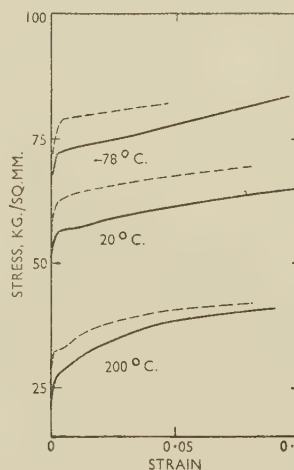


FIG. 3.—True-Stress/True-Strain Curves for Titanium at Various Testing Temperatures.

— Unirradiated. — — — Irradiated.

irradiation was roughly equal to that at  $-78^{\circ}$  C. The elongation before fracture of the irradiated specimens was only slightly less than that of the unirradiated specimen, however, in contrast with the behaviour at  $-78^{\circ}$  C.

The yield stress of both the irradiated and unirradiated specimens at  $200^{\circ}$  C. was considerably lower than at  $20^{\circ}$  C., and a yield point was observed in the irradiated, though not in the unirradiated, specimens (Fig. 2); at lower temperatures the yield of both the irradiated and unirradiated material was smooth. As a consequence of the yield point, the increase in yield stress produced by irradiation was considerably greater than the increase in ultimate tensile strength. The true-stress/true-strain curves (Fig. 3) illustrate the greater increase in flow stress of the irradiated specimens at low strains. The reduction in ductility consequent upon irradiation was only slight at this temperature.

The yield stress of both irradiated and unirradiated specimens was strongly dependent upon the testing temperature (Fig. 4), and this temperature-dependence has been observed for unirradiated titanium by several other workers. The increase in yield stress produced by an irradiation of  $5 \times 10^{19}$  neutrons/cm.<sup>2</sup>, however, was almost independent of the testing temperature between  $-80^{\circ}$  and  $+200^{\circ}$  C., being about constant at 8000 lb./in.<sup>2</sup> The ultimate tensile strength appeared to be less affected by irradiation at  $200^{\circ}$  than at  $20^{\circ}$  and  $-78^{\circ}$  C., and this behaviour was reflected by a smaller difference in flow stress at  $200^{\circ}$  than at  $20^{\circ}$  or  $-78^{\circ}$  C. The constancy of the increase in yield stress with testing temperature was misleading, as the large increase in yield stress at  $200^{\circ}$  C., due to irradiation, appeared to be attributable to the development of a yield point absent at other temperatures. Two effects were operating, therefore: a temperature-dependent increase in yield and flow stress, which was smaller at  $200^{\circ}$  than at  $20^{\circ}$  C.,

and the development of a yield point at 200° C., absent at 20° C.

The elongation before fracture was only slightly temperature-dependent in unirradiated material (Fig. 4), decreasing from 10.5 to 9.5% between -80° and +200°

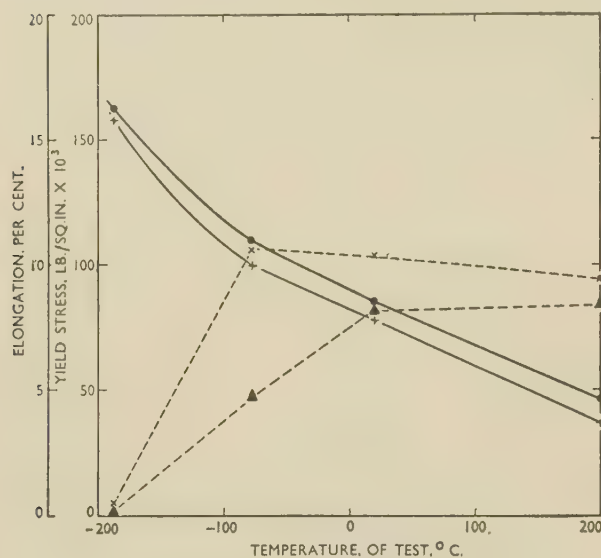


FIG. 4.—Elongation and Yield Stress of Titanium as a Function of Testing Temperature.

KEY  
 • Irradiated } Yield stress.  
 + Unirradiated }  
 ▲ Irradiated } Elongation.  
 × Unirradiated }

C. The elongation before fracture of irradiated material increased from 4.7 to 8.2% between -80° and +20° C., however, and was almost independent of temperature between 20° and 200° C. At all temperatures, the elongation to fracture of the irradiated material was less than that of the unirradiated, but from 20° to 200° C. the difference was small after  $5 \times 10^{19}$  neutrons/cm.<sup>2</sup>

The strain-hardening exponent,  $n$ , defined by the relation:

$$\sigma' = A\delta^n$$

was reduced by irradiation at 20° and 200° C. (Table II). No determination of  $n$  for irradiated specimens at -78° C. was possible owing to the small elongation before fracture. The reduction in the strain-hardening exponent was reflected in the smaller difference between the yield stress and the ultimate tensile strength after irradiation.

## 2. ZIRCONIUM

Heavily cold-worked zirconium was tested at temperatures between 20° and 200° C. after irradiation, and the average stress/strain curves at the various temperatures are given in Fig. 5 and Table III. The same general features were observed at all temperatures.

At 20° C. plastic flow began in both the irradiated and unirradiated specimens at about the same stress, but the unirradiated material work-hardened more rapidly than the irradiated, so that up to about 2.7% extension the irradiated specimens were slightly softer than the unirradiated. At higher extensions, however, the curves

crossed over and the irradiated specimens hardened at a greater rate than the unirradiated. This behaviour was repeated at the other testing temperatures, 90°, 160°, and 200° C., but the extension at which the curves crossed decreased with increasing temperature from 2.7%

TABLE III.—Tensile Tests on Zirconium.

(Limits of experimental results with the average values in parentheses.)

Temperature of Test, °C.	Unirradiated or Irradiated	Yield Stress, lb./in. <sup>2</sup> × 10 <sup>3</sup>	Ultimate Tensile Strength, lb./in. <sup>2</sup> × 10 <sup>3</sup>	Elongation, %
20	Unirradiated	103.2-110.8 (107.0)	117.7-129.4 (123.5)	3.2-3.8 (3.5)
	Irradiated	105.3-106.7 (106.0)	123.2-125.3 (124.3)	4.0-4.3 (4.2)
90	Unirradiated	102.7	115.0	2.7
	Irradiated	95.5	115.2	3.44
160	Unirradiated	90.8-93.6 (92.2)	98.4-102.5 (100.5)	1.7-2.0 (1.9)
	Irradiated	90.1-90.2 (90.1)	106.2-106.2 (106.2)	2.7-3.0 (2.9)
200	Unirradiated	86.4-86.7 (86.6)	89.8-92.3 (91.1)	2.0-2.1 (2.1)
	Irradiated	82.3-82.3 (82.3)	92.3-92.9 (92.6)	2.7-2.7 (2.7)

at 20° C. to 1.2% at 200° C. The elongation before fracture of the irradiated specimens was at all temperatures greater than that of the unirradiated (Fig. 6); at 200° C. the average elongation of the irradiated specimens was 2.7%, whereas that of the unirradiated was only 2.0%. The increase in elongation after irradiation did not appear to be markedly temperature-sensitive.

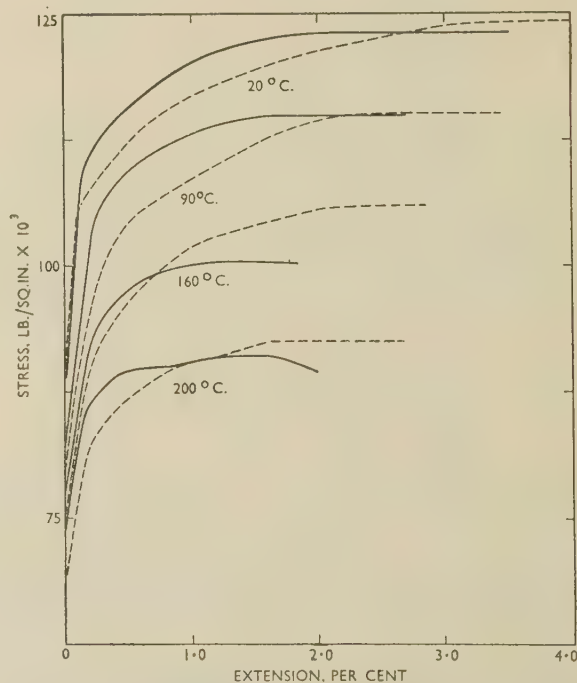


FIG. 5.—Average Stress/Strain Curves for Zirconium at Various Testing Temperatures.

———— Unirradiated.      - - - - - Irradiated.

The low values of elongation observed were due, of course, to the initial heavily cold-worked state of the material.

The yield stress of both the irradiated and unirradiated



specimens was, strongly dependent upon the testing temperature, being (unirradiated) about 105,000 lb./in.<sup>2</sup> at 20° C. and falling almost linearly to 83,000 lb./in.<sup>2</sup> at 200° C. The yielding of all specimens was smooth, and no evidence of any yield point was observed in either the irradiated or unirradiated material.

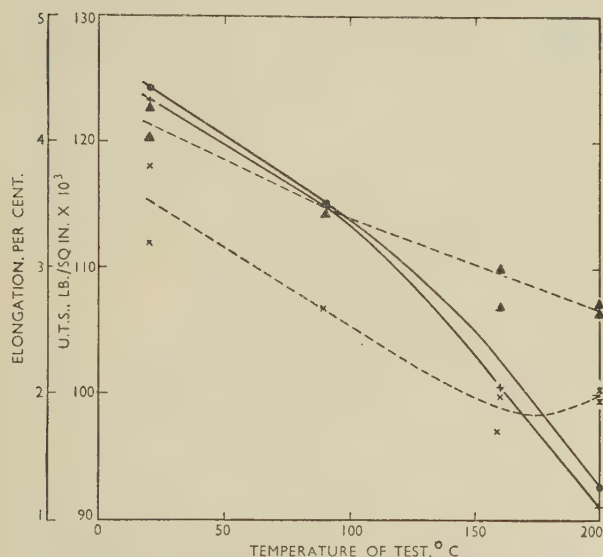


FIG. 6.—Elongation and Ultimate Tensile Strength of Zirconium as a Function of Testing Temperature.

KEY  
 • Irradiated } U.T.S.  
 + Unirradiated }  
 ▲ Irradiated } Elongation.  
 × Unirradiated }

The ultimate tensile strength was increased by the irradiation at all temperatures of testing between 20° and 200° C., and in this respect the behaviour was similar to that of annealed material. The amount of the increase (approx. 1500 lb./in.<sup>2</sup>) was less than would be expected in fully annealed zirconium.

## IV.—DISCUSSION OF RESULTS

### 1. TITANIUM

The titanium used was of normal commercial purity and, with the possible exception of the ductility, its properties unirradiated compare reasonably well with American work on commercial-purity material of similar structure. The yield-stress/temperature curve (Fig. 4) is very similar in shape to that given by Rosi, Perkins, and Alexander,<sup>6</sup> except that the yield stress is about 3000 lb./in.<sup>2</sup> higher throughout the temperature range in the present work. The elongation, however, is lower than in the work of Rosi, Perkins, and Alexander; about 10% instead of 27%. The difference between these results is probably due to the grain-size, and to the greater purity of the titanium used by the American workers.

The variation in yield stress with testing temperature appears to be roughly linear between -80° and +200° C. This behaviour has been previously noted by Rosi, Perkins, and Alexander and other workers, and strain-

ageing phenomena have been observed at high rates of test between -80° and +200° C. At the rate of test of the experiments now recorded, however, no yield phenomena were observed in the unirradiated material. The reason for the large linear temperature-dependence of the yield stress in unirradiated titanium has not been established, but it may be merely fortuitous, since after correction of the yield stresses for the variation in Young's modulus, the linear relationship with temperature is no longer obeyed.

The increase in the yield and flow stress of titanium on irradiation is in general agreement with results obtained on other metals. The variation of the increase with testing temperature is interesting, in that the apparent increase in yield stress is independent of testing temperature between -80° and +200° C. Examination of the flow-stress curves, however, reveals that this is due to two opposing effects. The increase in flow stress produced by irradiation is less at the higher testing temperatures, but a yield point is developed at the higher temperature which is absent at the lower. The existence of this yield point at 200° C. indicates that a defect produced by irradiation becomes mobile between 20° and 200° C. and migrates to the dislocations and anchors them. No experimental information is available for defect migration in titanium, but for the temperature range involved, and by analogy with other metals, it is probable that the defects are vacancies.<sup>7</sup> The yield point cannot be due solely to the effect of temperature on the yield, as in this case the reverse would be expected, i.e. a marked yield point at low temperatures becoming less pronounced as the temperature is raised. The development of a yield point on annealing cold-worked copper at a temperature where the vacancies produced by the deformation are mobile, has been observed by Pry and Hennig<sup>8</sup> and by Blewitt, Redman, and Sherrill,<sup>9</sup> and it is possible that the same phenomenon is occurring in irradiated titanium. At the lower temperatures, the yield was quite smooth in all cases.

The decrease in elongation before fracture after irradiation (Fig. 4) is a general phenomenon observed in all irradiation studies on well-annealed metals. It is interesting, however, that the elongation is reduced by the greatest extent at -80° C. The elongation before fracture is closely associated with the value of the strain-hardening exponent  $n$ . The lower the value of  $n$ , the greater the tendency of the specimen to become unstable and neck down in one place instead of extending uniformly all along its length. The considerable reduction in  $n$  produced by irradiation is apparent from Table II.

### 2. ZIRCONIUM

The behaviour of the heavily cold-worked zirconium under irradiation differs considerably from that of annealed titanium, and this is attributed to the effect of the cold work. The zero effect on the yield stress and the reduction in the flow stress at low extensions contrasts markedly with the increased yield stress of annealed titanium on irradiation. The rate of work-hardening of the irradiated zirconium was initially lower than that of unirradiated material, but with increasing strain the rates approached each other, became equal, and then the irradiated material hardened more rapidly. This is in marked contrast with the behaviour of annealed

metal, where the rate of work-hardening was lower for the irradiated material at all strains. The most striking difference, however, is that the elongation before fracture of heavily cold-worked material increased on irradiation, whereas that of annealed material decreased. The increased elongation before fracture was associated with the greater rate of work-hardening of the irradiated material at the higher strains.

In the cold-worked material, the effect of irradiation appears to be, in general terms, to anneal out a part of the cold-work damage, replacing it by irradiation damage. The mechanism whereby this annealing process can occur is not clear; it may be due to the presence of thermal or displacement spikes, or to recovery due to condensation of point defects producing the same effects as the thermal vacancies during high-temperature annealing. This behaviour implies, however, that the defects condense on dislocations in an organized rather than in a random manner, a postulate difficult to accept. This difficulty is avoided if the defects are able to migrate along the dislocations at the irradiation temperature, and under these conditions a large excess of defects of one sign could produce substantial dislocation recovery. In the absence of an established model of the atomic configuration responsible for the changes in mechanical properties, these considerations must remain speculative.

The number of lattice displacements produced for each primary collision between a 1-MeV. neutron and a lattice atom is approximately 400 in titanium and zirconium, and the total concentration of defects produced in each metal during an irradiation of  $5 \times 10^{19}$  neutrons/cm.<sup>2</sup> is roughly  $6 \times 10^{-2}$ .

Alternatively, the recovery of cold-worked metals during irradiation may be due to the formation of local hot-spots during the irradiation—the thermal and displacement spikes. The thermal spikes can be shown to be incapable of producing the required recovery,<sup>10</sup> the duration of the spike being too short to allow sufficient movement of the defects. According to Brinkman,<sup>11</sup> local melting of the crystal lattice occurs when the energy of a knock-on falls below a critical value, and calculation of the number of Brinkman displacement

spikes formed by the irradiation indicates that each lattice atom has been within a Brinkman spike on average just over twice. This calculation ignores the effect of those displacement spikes formed with initial energies lower than the critical value of 9000 eV. postulated by Brinkman. These lower-energy spikes would, if melting occurred, produce a still larger effect. If annealing out of the cold work occurs within the displacement spikes, then it must be postulated that recovery of irradiation damage may also occur, since it is known that irradiation damage recovers in several metals at a faster rate than cold work at any given temperature. This recovery process will result in a saturation in the effect of irradiation at a dose dependent upon the relative effectiveness of the atomic defects formed and the recovery produced by the Brinkman spikes associated with a single neutron.

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# THE PRESSURE FOR THE COLD EXTRUSION OF LUBRICATED ROD THROUGH SQUARE DIES OF MODERATE REDUCTION AT SLOW SPEEDS\*

1762

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## SYNOPSIS

When pure lead is used in extrusion experiments, an empirical relationship between the pressure and the reduction may easily be obtained and also a measure of the mean strain imparted to the product, uncomplicated by strain-hardening effects. When the form of the strain-hardening characteristic of other metals is not similar to that of lead, it is shown that, by utilizing this characteristic to give a mean yield stress over the range of strain predicted by the empirical expression for lead, the pressure for its extrusion may then be predicted to better than  $\sim 7\%$ .

## I.—INTRODUCTION

INVESTIGATIONS into the cold extrusion of cylindrical rods usually focus on two aspects of the process: (a) the autographic diagram, i.e. the variation of the extrusion load with punch displacement, and (b) observations of the manner of deformation of the metal during its flow. In this paper (a) only is considered.

The extrusion operation contains many variables and therefore, to obtain a basic understanding of the process, attention is usually restricted to the five fundamental factors: reduction, frictional and geometrical boundary conditions, the strain-hardening characteristic of the material, and the speed of the operation. The present investigation has been concerned only with pressure as a function of reduction and the strain-hardening characteristic when the other factors have remained unchanged.

The first rational relationship between extrusion pressure,  $p$ , and reduction of area,  $r$ , appears to have been put forward by Siebel and Fangmeier<sup>1</sup> and was based on the assumption of uniform deformation. It was assumed that:

$$p = k' \log_e 1/(1 - r) \quad \dots \quad (1)$$

where  $k'$ , the "resistance to deformation . . . depends on temperature and . . . speed of extrusion". This expression was not related to a particular length of slug, but for direct extrusion it was modified to include a term to allow for friction between the *total* length of the slug and the container wall. These authors also proposed the same expression for use in the case of reverse extrusion.

The second major contribution to an understanding of this process was that of Hill,<sup>2</sup> who provided some theoretical solutions for the extrusion of an ideal non-hardening material under conditions of plane strain. Hill suggested that the pressure for plane strain and axisymmetric extrusion for equal reductions of area may be expected to be approximately the same. Whilst Hill's

statement is correct as regards order of magnitude, it is generally found that the pressure, as calculated for the plane-strain extrusion, consistently underestimates that for the axis-symmetric case.<sup>3</sup>

Regarding the possibility of obtaining exact mathematical solutions for the axis-symmetric case, Hill has stated that "they are at present beyond reach".<sup>4</sup> It is for these reasons that the present author has adopted an inductive and empirical approach.

## II.—THE AUTOGRAPHIC DIAGRAM

The extrusion of cylindrical rod from a solid cylindrical slug through square dies is usually effected by either the direct or reverse method. The drawings of the apparatus used, shown in Figs. 1 (a) and (b), clearly illustrate the mode of operation. In direct extrusion the punch and product travel in the same direction; in the reverse method they travel in opposite directions.

Autographic diagrams showing the variation of punch load with punch travel for these two processes for comparatively slow-speed work are of the form shown in Fig. 2, provided that the material does not undergo rapid strain-hardening. These diagrams consist of three principal phases:

### (1) *The Coining Phase*

There is a rapid build-up of pressure caused by the initial compression of the slug, which exactly fills and expands the container; there is also a small amount of extrusion of relatively unstrained material.

### (2) *The Steady-State Phase*

As the punch moves over this range, extrusion proceeds steadily, the total load in the case of direct extrusion continuously decreasing because the frictional load due to the relative motion of slug and container wall is decreasing. In reverse extrusion, no such steady decrease

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occurs, because there is no relative motion between the slug and the container wall; the top of the extrusion diagram is almost flat.

### (3) The Unsteady-State Phase

Beyond a certain point, the extrusion load begins to decrease fairly rapidly; this point is called the *coring*

the whole of the pressure pad, and the term "extrusion pressure", as usually understood, ceases to be meaningful, since the area over which the extrusion load acts is no longer obvious. Continued extrusion beyond the coring point extends the size and depth of the hole and may result in a worthless product. The load continues to decrease to a minimum, but ultimately increases at a rapid rate. From this analysis of the diagram, the true extrusion pressure is taken as that prevailing at the onset of coring, and in the experimental results shown below this point is clearly marked.

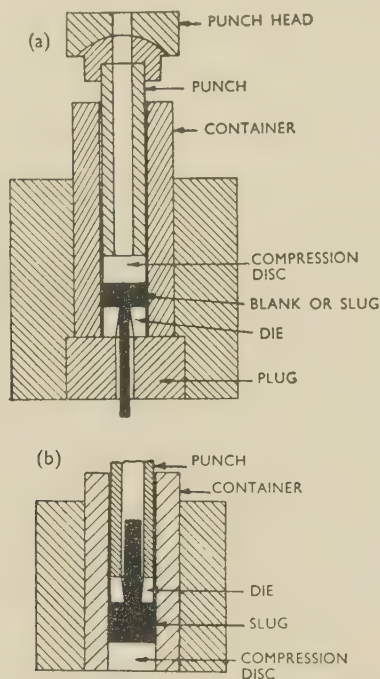


FIG. 1.—Extrusion Apparatus Set Up for (a) Direct Extrusion; (b) Reverse Extrusion.

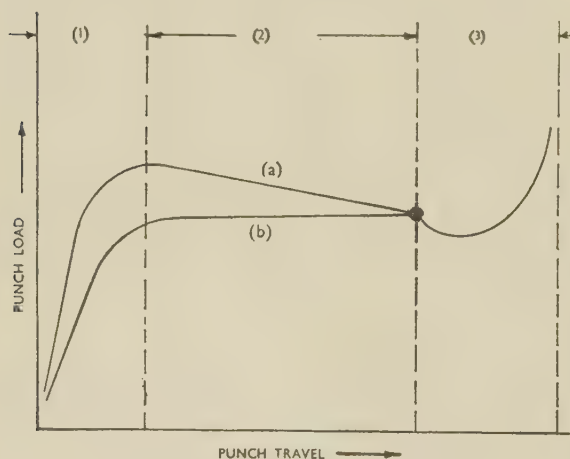


FIG. 2.—Idealized Autographic Diagrams for: (a) Direct Extrusion; (b) Reverse Extrusion.

(1) Coining phase; (2) steady-state phase; (3) unsteady-state phase.

• Coring point.

point and is clearly shown in Fig. 2. If an extrusion test is interrupted when this point of accelerated load decrease is reached and the slug is examined, it will be observed that a circular hole is forming on the axis of the slug.<sup>5</sup> The extrusion load is no longer carried over

## III.—EXPERIMENTAL

### 1. APPARATUS

The form and details of the experimental apparatus, originally designed by Chang,<sup>6</sup> are shown in Fig. 1. The container is a compound cylinder of 1 in. bore, housing various dies and compression discs, and the long bore serves also as a guide for the punch. The lower end is closed by a threaded plug on which either a die (direct extrusion) or compression disc (reverse extrusion) rests. The outer cylinder is made from a piece of gun-barrel and the inner sleeve from specially heat-treated high-speed steel. The container is designed to withstand internal radial pressure of 60 tons/in.<sup>2</sup>.

The punch is made of 2½% nickel-chromium-molybdenum steel, heat-treated to about 100 tons/in.<sup>2</sup> tensile strength, and contains a bore 0.4 in. in dia. which serves to pass extruding metal in the reverse process, if required. The load is applied to the punch through its spherical head, thereby ensuring axial loading.

The dies and compression discs are made from high-carbon, high-chromium steel, heat-treated by the makers and ground to the required dimensions. All the dies, which are square-edged, were lapped and polished.

The autographic diagrams were obtained by using the apparatus in a testing machine operated at a steady speed of 0.1 in./min. The machine beam was manually controlled and balanced, and readings of the current load at 1-min. intervals were noted. The machine cross-head compelled the punch to advance at a steady rate, so that by means of a stop-watch it was possible to construct the autographic diagram from readings of the punch travel and the punch load, the slug being of known initial length.

### 2. COMPRESSION-TEST PROCEDURE

Compression tests were performed on the materials extruded, two specimens of each being compressed to a logarithmic strain greater than 3. The tests were carried out at the same speed as that of the extrusion, i.e. 0.1 in./min. The compression platens were of hardened metal (V.P.N. 649), lapped and polished to a surface finish of 2–3 micro-in. The strain measurement was made by means of two dial-gauges placed on stands on either side of the specimen.

The specimens used were originally of 1 in. dia. and 1.5 in. long, this length having been determined as short enough to avoid tilting of the specimen during compression. Grooves were turned in the ends of the specimens to facilitate retention of the lubricant; 60 grooves, 0.01 in. deep, spaced at 30 to the in. dia., were used.<sup>7</sup> It is believed that the grooving had a negligible effect on



the length during compression, especially as the magnitude of the strains attained was so large.

The procedure in a test was first thoroughly to lubricate the ends of the specimen, carefully ensuring that the lubricant, graphite in tallow, had been forced well down into the grooves. A load of about 100 lb. was applied to the specimen when centred on the platens, to align it and squeeze out superfluous lubricant. The load was then taken off and the dial-gauges set.

Simultaneous readings of load and of both dial-gauges

dia. and compressed to a height of 0.35 in. Again it was turned down, this time to 0.563 in. dia. The final height of the compressed specimen was 0.075 in. It was not found necessary to turn fresh grooves after each stage of the compression.

### 3. MATERIALS

The materials extruded were: (a) "Tadanac" pure lead (supplied as extruded bar), and (b) super-pure aluminium, in the form of 1-in.-dia. slugs about 1.3 in. long. Before the lead was used it was heavily hammered to refine the grain-size. No heat-treatment was given to the aluminium.

## IV.—EXPERIMENTAL RESULTS

### 1. AUTOGRAPHIC DIAGRAMS

The later portions of the autographic diagrams, for the direct extrusion of both materials through each of five square dies giving a different reduction, are shown in Figs. 3 (a) and (b). From these the true extrusion load is read off and recorded in Table I. It will be observed that this true load for the lead is fairly clearly defined, but it is less obvious in the case of aluminium. Repeated tests on these lubricated specimens generally agreed to better than ~3%.

### 2. TRUE-STRESS/ LOGARITHMIC-STRAIN CURVES

These curves, as calculated from the compression tests for both materials, are shown in Fig. 4 as (a) and (b). The curves for two tests made on each material were almost identical.

## V.—INTERPRETATION OF EXPERIMENTAL RESULTS

By considering a non-hardening material of which the uniaxial yield stress is  $Y$ , it can easily be shown that the final pressure required to alter the dimensions of a cylindrical block from height  $h_0$  to  $h$ , and respective cross-sectional area from  $A_0$  to  $A$ , is given by:

$$p = Y \log_e h_0/h \quad . \quad . \quad . \quad (1)$$

This expression was first used by Fink and later by Siebel and Fangmeier<sup>8</sup> in analysing the results of their extrusion experiments. Expression (1) assumes that the change of shape is achieved by a process of homogeneous

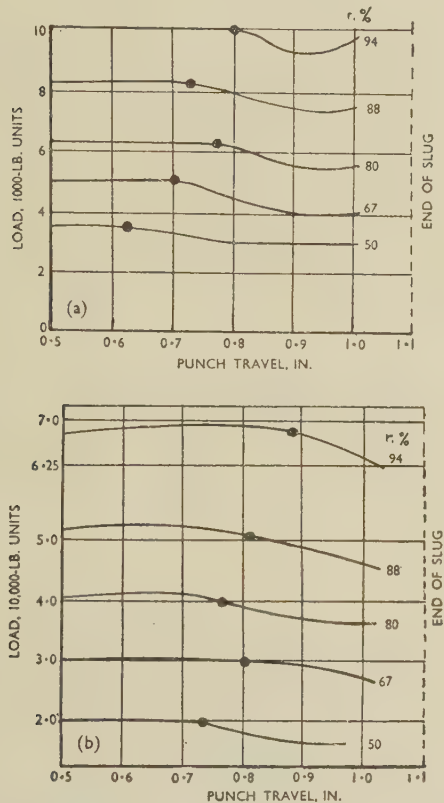


FIG. 3.—Later Portions of Autographic Diagrams for: (a) Pure Lead; (b) Super-Pure Aluminium.

were recorded after each 0.025 in. travel of the cross-head.

The first stage of compression continued until the specimen height was altered to 0.75 in. and its dia. to 1.25 in. The specimen was then turned down to 0.80 in.

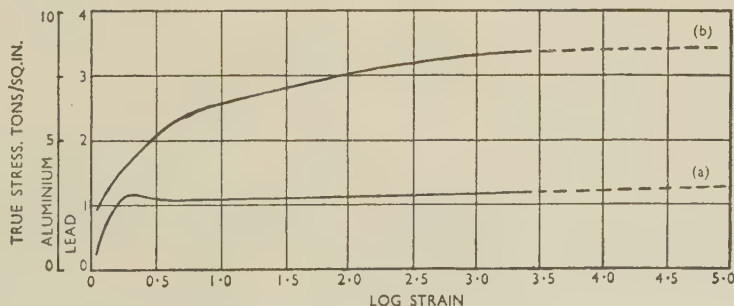


FIG. 4.—True-Stress/Logarithmic-Strain Curves for (a) Pure Lead; (b) Super-Pure Aluminium.  
— Experimental. — — — Extrapolation.

deformation and, as stated above, in order to correlate experimental and empirical expressions, these latter workers used:

$$p = c Y \log_e A_0/A \quad . \quad . \quad . \quad (2)$$

$c$  being an empirical constant.

Equation (1) states, in effect, that the plastic work done per unit volume of that material is equal to the product of the uniaxial yield stress and the logarithmic strain imparted to it. It is now proposed that for a non-hardening material it be assumed that:

$$p/Y = a + b \log_e 1/(1-r) \quad . \quad . \quad (3)$$

where  $a$  and  $b$  are as yet unspecified constants; the right-hand side of equation (3) is to be regarded as the mean strain imparted to extruded lengths of slug. The origin and justification of this approach is to be found in the theoretical and experimental treatment of the case of the plane-strain extrusion.<sup>5</sup> For this analogous case, an equation similar in form to (3) has been derived theoretically and confirmed experimentally. The case of the axi-symmetrical extrusion of the ideal, non-hardening material has not yet been solved theoretically,<sup>4</sup> but when this is achieved, it should be possible to summarize the results theoretically in a manner similar to that assumed in (3). However, for several reasons such a solution will be of limited value when its experimental confirmation is sought, e.g. because it will remain to give meaning to  $Y$  for a non-hardening material, &c.<sup>5</sup> In effect, the proposed methods attempt to anticipate such difficulties as are already apparent in theoretical solutions by substituting an experimental approach based, however, on contact with a theoretically exact analogous case.

It follows then that, if expression (3) is accepted, by performing experiments on non-hardening materials it should be possible to deduce reasonable estimates of this mean strain for each value of  $r$  from measurements of  $p$  and  $Y$ . In effect, we should be determining  $a$  and  $b$  empirically. Pure lead, as is evident from Fig. 4 (a), simulates such a non-hardening material, and from experiments on this material, the value of  $p/\bar{Y}$  for each reduction may be obtained (see Table I).

TABLE I.—*Experimental Results for Extrusion of Pure Lead.*

Fractional Reduction, $r$	Load, lb.	Pressure, $p$ , tons/in. <sup>2</sup>	$\bar{Y}$ , tons/in. <sup>2</sup>	Experimental Value $p/\bar{Y}$	Predicted Value $p/\bar{Y}$
0.50	3,600	2.05	1.12	1.85	1.85
0.667	5,000	2.85	1.13	2.5	2.45
0.80	6,250	3.55	1.14	3.1	3.2
0.88	8,350	4.75	1.14	4.15	4.0
0.94	10,000	0.70	1.15	4.95	5.0

If values of  $p/\bar{Y}$  are plotted against  $r$  and the best straight line drawn through the points, it is found that:

$$p/\bar{Y} = 0.8 + 1.5 \log_e 1/(1-r) \quad . \quad . \quad (4)$$

When cold extruding a strain-hardening material, it is well known that individual elements are hardened

differently, since the process is one of inhomogeneous deformation and no simple equation can be formulated to take account of this. It is suggested that the mean overall strain imparted to the block may be expected to be closely approximated by that undergone by a non-hardening material under similar conditions, and hence that the differential hardening is taken account of by a value of  $\bar{Y}$ .  $\bar{Y}$  is the average value of the true stress over the range of logarithmic strain from 0 to  $(0.8 + 1.5 \log_e 1/(1-r))$ , as given by the ordinates in Figs. 4 (a) and (b),  $p$  being the value appropriate to the extrusion being performed.

This method has been applied to the experimental values obtained for aluminium and the results of the calculation,  $p/\bar{Y}$ , are shown in Table II. The values so derived are seen to be in remarkably close agreement with those predicted by expression (4).

TABLE II.—*Experimental Results for Extrusion of Super-Purity Aluminium.*

Fractional Reduction, $r$	Load, lb.	Pressure, $p$ , tons/in. <sup>2</sup>	$\bar{Y}$ , tons/in. <sup>2</sup>	Experimental Value of $p/\bar{Y}$	Predicted Value of $p/\bar{Y}$
0.50	19,500	11.1	6.1	1.8	1.85
0.667	30,100	17.1	6.5	2.6	2.45
0.80	38,500	21.9	6.9	3.15	3.2
0.88	51,000	29.0	7.1	4.05	4.0
0.94	67,500	38.4	7.5	5.1	5.0

## VI.—FURTHER EXPERIMENTS

More recent experiments, employing the same apparatus, procedure, and method of analysing the results as those described above, have been carried out by Mr. L. C. Dordeja at Sheffield University,<sup>9</sup> on new batches of pure lead and super-pure aluminium and on a lead-0.065% tellurium alloy and pure tin. The autographic diagrams are reproduced in Fig. 5, and the corresponding stress/strain curves in Fig. 6. The collected results are

TABLE III.—*Experimental Results for the Extrusion of Lead, Tin, and Aluminium.*

Material	Fractional reduction, $r$	Load, tons	Pressure, $p$ , tons/in. <sup>2</sup>	$\bar{Y}$ , tons/in. <sup>2</sup>	Experimental Value of $p/\bar{Y}$	Predicted Value of $p/\bar{Y}$
Pure lead	0.75	2.78	3.54	1.30	2.72	2.88
	0.86	3.8	4.85	1.31	3.71	3.75
	0.938	5.15	6.55	1.31	5.00	4.97
Tellurium lead (0.065% Te)	1.75	4.5	5.75	1.94	2.96	2.88
	0.86	5.9	7.5	1.96	3.83	3.75
	0.938	7.95	10.1	1.97	5.12	4.97
Pure tin	0.75	5.6	7.15	2.41	2.96	2.88
	0.86	7.55	9.63	2.54	3.79	3.75
	0.938	11.0	14.0	2.72	5.11	4.97
Super-pure aluminium	0.75	15.0	19.1	6.44	2.95	2.88
	0.86	21.25	27.1	6.80	3.97	3.75
	0.938	31.0	39.5	7.35	5.33	4.97

given in Table III and confirm the approximate correctness of expression (4) and the method of evaluating the quantity  $p/\bar{Y}$ .



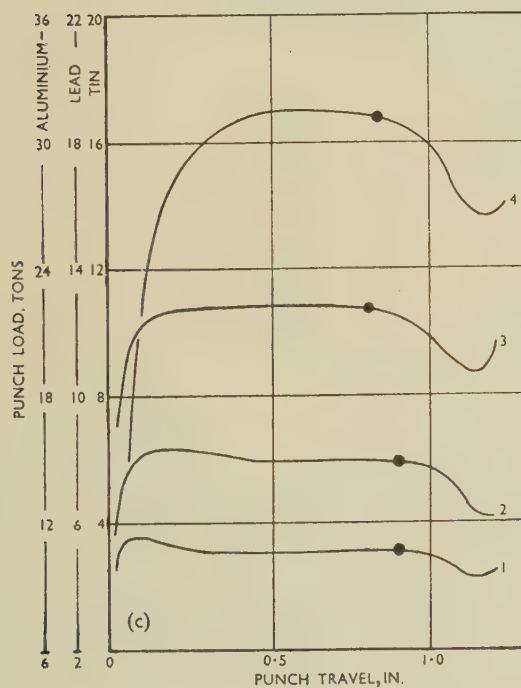
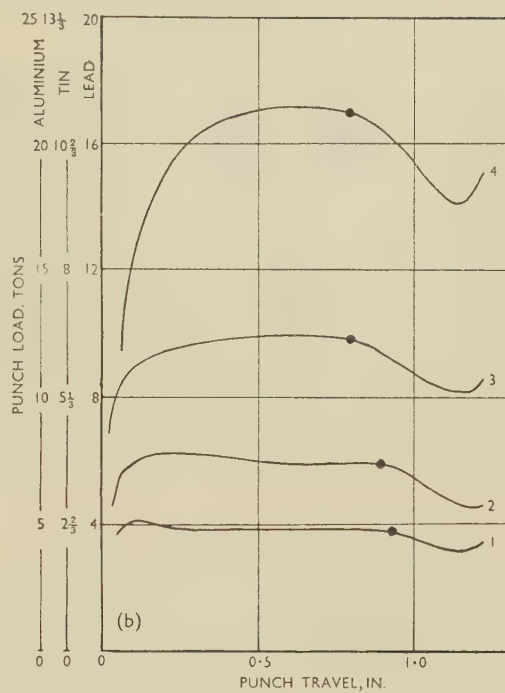
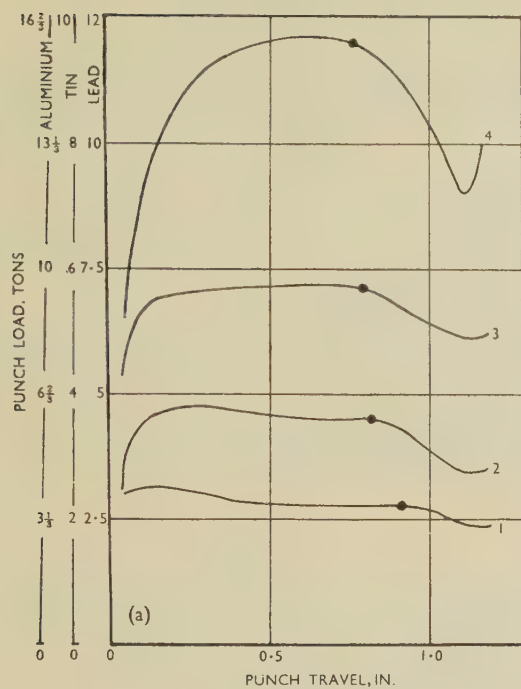
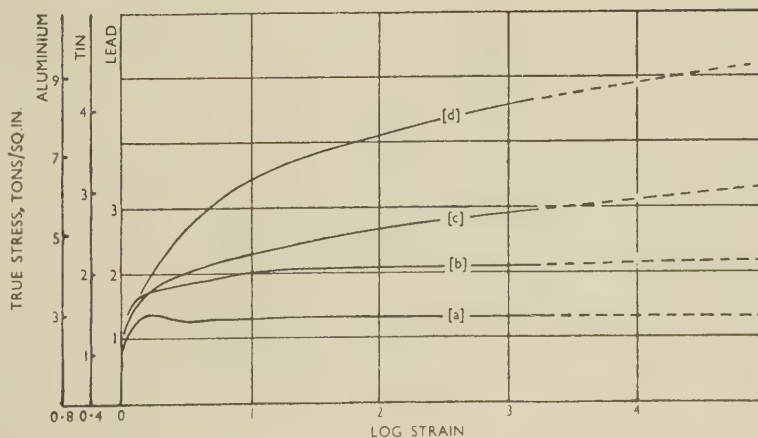


FIG. 5.—Autographic Diagrams for : (1) Pure Lead; (2) Lead-0.065% Tellurium Alloy; (3) Pure Tin; (4) Super-Pure Aluminium.

(a)  $r = 0.75$ ; (b)  $r = 0.86$ ; (c)  $r = 0.938$ .

FIG. 6.—True-Stress/Logarithmic-Strain Curves for: (a) Pure Lead; (b) Lead-0.065% Tellurium Alloy; (c) Pure Tin; (d) Super-Pure Aluminium.

— Experimental.  
 - - - Extrapolation.



## VII.—CONCLUSIONS

The pressure to cold extrude lubricated cylindrical rod through square dies can be predicted to better than 7% by using the empirical expression (4) above, when a true-stress/logarithmic-strain curve for the material is available.

The approach of this paper is characterized by two main features:

(1) The abandonment of dependence upon any form of theoretical prediction of  $p/\bar{Y}$  and the substitution of a purely empirical and inductive method of investigation, having its rational basis in the study of plane-strain extrusion.

(2) An assumption that the empirical parameters for given conditions are independent of the strain-hardening characteristic of the material.

## ACKNOWLEDGEMENTS

The author wishes to thank Mr. L. C. Dordeja, for providing corroborative experimental evidence, and B.I.S.R.A., for their financial support of the work.

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## Discussion

## Lattice Spacings of the Silver-Rich Solid Solution Containing Magnesium and Antimony

By R. B. HILL and H. J. AXON

(*Journal*, this vol., p. 109).

Mr. L. M. CLAREBROUGH, \* B.Met.E., M.Eng.Sc. (Member), and Mr. J. F. NICHOLAS \*: We were surprised, on looking at Fig. 1 and the accompanying discussion (Section III.3), to find that our results seemed to be at variance with the results of the authors and with those of Andrews and Hume-Rothery. However, on investigation, it became obvious that the authors had plotted our result of 4.111 Å, the lattice parameter of the disordered alloy, directly as 4.111 kX, without applying the conversion factor. In actual fact, our figure was derived from a value of 4.103 kX, calculated by using the same wavelengths as those used by the authors. As shown in Fig. A, this value is in agreement with those of the authors and of Andrews and Hume-Rothery. It may be noted here that the lattice parameter of the ordered alloy at this composition is significantly less, viz. 4.100 kX.

THE AUTHORS (*in reply*): We are grateful to Messrs. Clarebrough and Nicholas for making available this more detailed account of their findings and hope that they will forgive our misunderstanding of their original report, particularly as we are now in complete agreement factually.

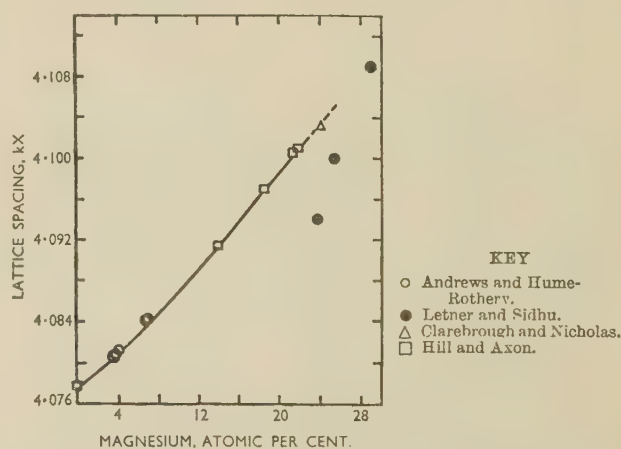


FIG. A.—Lattice Spacing/Composition Relationship for the Silver-Rich Silver-Magnesium Solid Solution.

\* Division of Tribophysics (C.S.I.R.O.), University of Melbourne, Australia.



By ROBERT J. TEITEL, † Sc.D.

## SYNOPSIS

In order to confirm the conclusions concerning the liquid immiscibility in the lead-uranium system reached in an earlier paper (*Trans. Amer. Inst. Min. Met. Eng.*, 1952, **194**, 397), the experiments on which these conclusions were founded are described in greater detail. New data on the solubility of uranium in lead, obtained by a filtration technique, and on the crystal structure of UPb, obtained by neutron diffraction, are also presented. UPb has a body-centred tetragonal cell with  $c/a = 0.961$ ,  $a = 11.04$  Å., and contains 48 atoms. The density is estimated to be 13.7 g./c.c. A discrepancy between the values for the cell size of UPb<sub>3</sub>, as determined by Frost and Maskrey (*J. Inst. Metals*, 1953-54, **82**, 171) and by the present author, is discussed. According to present work,  $a = 4.791$  Å. and the density = 12.98 g./c.c.

## I.—INTRODUCTION

Frost and Maskrey<sup>1</sup> have expressed some doubts about the existence of the high-temperature liquid immiscibility in the uranium-lead system reported by the present

## II.—LIQUID-IMMISCIBILITY REGION

The evidence for immiscibility was based essentially on two types of experiment. One represented an attempt to produce a high-uranium alloy (containing more than

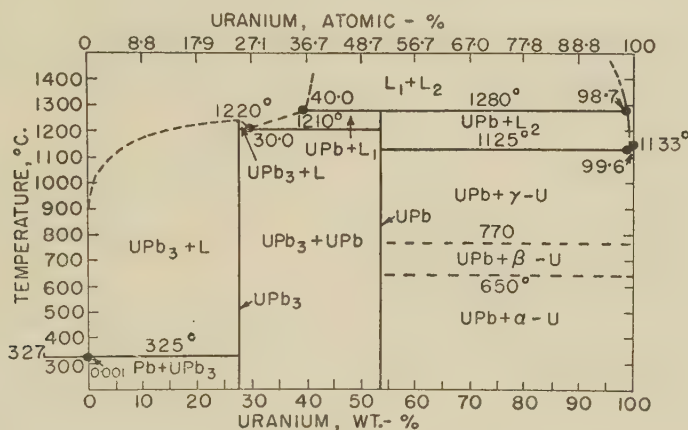


Fig. 1.—The Uranium-Lead Phase Diagram. (Teitel.<sup>2</sup>)

author<sup>2</sup> (Fig. 1). Their arguments were based on the following premises:

(a) The experimental evidence for immiscibility was weak and could be explained by simple gravitational separation.

(b) They themselves found a thermal arrest at 1190° C. for a 15 at.-% lead alloy. This was interpreted as a liquidus point on a somewhat flat liquidus curve.

(c) The whole idea of a syntectic reaction at these compositions did not seem reasonable.

In the following sections the experimental findings expressed in Teitel's earlier paper are described in greater detail. At the same time, more recent data concerning the solubility of uranium in lead and neutron-diffraction experiments on the crystal structure of the intermetallic compound UPb are presented.

40 wt.-% uranium) by melting uranium and lead at a high temperature. The other type of experiment involved the production of a homogeneous alloy at a lower temperature, microscopic examination, heating the alloy to high temperatures, and observing the separation of liquid.

## 1. ALLOY PREPARATION

As explained in the earlier paper,<sup>2</sup> many attempts at producing alloys containing more than 40 wt.-% uranium failed because the uranium in excess of 40% separated out. Attempts were made to invert and remelt the alloys without success. The resulting phase separation was the same, whether the uranium was in the form of bars or chips heated to a temperature above 1280° C. However, it was eventually found that uniform high-

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uranium alloys could be produced by heating the alloy to a temperature between 1220° and 1280° C.

Fig. 2 is a sketch of a typical cross-section of ingots produced at high temperatures (above 1280° C.). The upper section (lead-rich) usually contained 35–45 wt.-% uranium, while the lower section (uranium-rich) con-

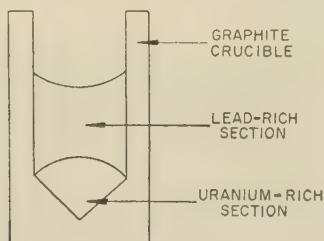


Fig. 2.—Typical Cross-Section of High-Uranium Alloys Containing More Than 40% Uranium, Prepared above 1280° C.

tained 98–99 wt.-% uranium with a clean meniscus between the two layers. Photomicrographs of the structure typical of the lead-rich and uranium-rich sections were given in the previous paper<sup>2</sup> (Figs. 3 and 6, respectively). The meniscus was invariably concave upward with no sign of a reaction interface, and usually broke cleanly with a bright shiny surface on the uranium-rich button and a light grey surface on the bottom of the lead-rich section. There was no sign of oxides or other phases to explain the interruption in alloying.

## 2. SEPARATION EXPERIMENTS

As the experience in producing alloys was not regarded as providing definite proof of immiscibility, experiments were designed which involved producing homogeneous alloys at lower temperatures, establishing that they were uniform, then heating them to high temperatures and trying to detect the phase separation by thermal, microstructural, and chemical analysis. This was done with several alloys, and essentially the same results were obtained.

For example, an alloy of 50 wt.-% uranium was prepared by melting uranium chips with lead at 1250° C. for 1 hr. in a graphite crucible. The resulting ingot appeared to be homogeneous (similar to Fig. 4 in reference 2). The alloy was then placed in a crucible in a furnace for thermal analysis. After the temperature had been raised to just below 1280° C., a cooling curve was taken. Only the eutectic reaction between  $UPb_3$  and  $UPb$  was detected at 1207° C. On the second heating cycle the temperature was taken well above 1280° C. and then allowed to fall. Reactions were detected at 1287°, 1210°, 767°, and 640° C. Examination of the alloy after this treatment showed that a uranium-rich button had separated out. Therefore the sequence of reactions was: a syntectic reaction at 1287° C., the eutectic reaction between  $UPb_3$  and  $UPb$  at 1210° C., and reactions at 767° and 640° C. being those of the solid transformation of uranium. By microscopic and chemical analysis it was confirmed that the lead-rich phase contained 41% uranium, while the uranium-rich button contained 98.5% uranium.

An attempt was made to establish the exact extent of the immiscibility region, but equilibration for long periods

at high temperatures could not be achieved owing to thermocouple failures. A value of ~40% uranium was given for the liquid composition on the lead-rich side. This, however, is not regarded as definitely established, as earlier attempts at producing alloys indicate that this point might be higher (up to 45% uranium).

## III.—SOLUBILITY OF URANIUM IN LEAD

Since the earlier work was carried out on the uranium-lead phase diagram, graphite filter crucibles have been developed for filtering alloys at high temperatures. This technique has been used on other similar systems and has provided a satisfactory check on solubilities determined by settling and siphoning techniques.

A crucible, having the cross-section shown in Fig. 3, was fabricated from an impervious grade of graphite (Graphitite, Graphite Specialties Corporation, Niagara Falls, New York) and a graphite frit (National Carbon Frit, grade 60). The latter was press-fitted into place.

The graphite filter crucible was outgassed in vacuum (1 $\mu$  Hg) at 1000° C. shortly before use. Uranium chips to make up a lead–2% uranium alloy were pickled in nitric acid, washed in water and acetone, dried, and placed on top of the filter. Lead was filtered through a Pyrex filter tube and cast into ingots. An ingot of lead was placed above the chips. The charged filter crucible

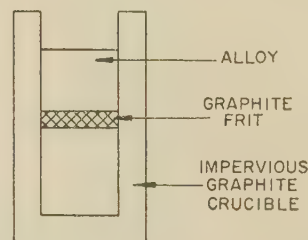


Fig. 3.—Section of Graphite Filter Crucible.

was then placed in a stainless-steel tube, which was attached to a vacuum gas manifold. After the tube had been evacuated below 1 $\mu$  Hg, the assembly was heated to 1000° C. for 1 hr. and then cooled to the desired filtration temperature, care being taken not to cool below that temperature. The alloy was held there for  $\frac{1}{2}$  hr. and filtered by admitting argon gas to a pressure of 20 lb./in.<sup>2</sup> The filtered liquid was collected in the bottom of the crucible and subsequently analysed for uranium. The results are listed below:

Temp., °C.	Solubility, % U
416	0.002
612	0.046
806	0.26
1000	0.59

The solubility data now given indicate that the solubility of uranium in lead is somewhat lower than that reported by Frost and Maskrey.<sup>1</sup> A line was drawn through the experimental points, taking into consideration the accuracy of the method. The heat of solution, determined from the slope of the line, was 17,900 cal./mole.



## IV.—CRYSTAL STRUCTURE OF UPb

Attempts at obtaining X-ray-diffraction data on the intermetallic compound UPb having failed, neutron-diffraction procedures were tried and found successful. Such techniques lend themselves to studies of pyrophoric compounds because the beam is more penetrating and is not readily absorbed in an oxide skin. Moreover, the specimen does not need to be pulverized and a 1-in.-dia. ingot of alloy can be used, thus reducing the handling

was obtained. The resolution of the spectrometer was approximately  $20'$  of angle  $2\theta$  in the Bragg diffraction equation. The spacings were calculated and are tabulated in Table I.

Chemical analysis of samples from the top and bottom of the ingot, respectively, placed the composition at 39–45% uranium. Evidently, some of the uranium hydride powder was blown out of the crucible when the vacuum pumps were turned on. Microstructural examination of this particular alloy was unsuccessful. However,

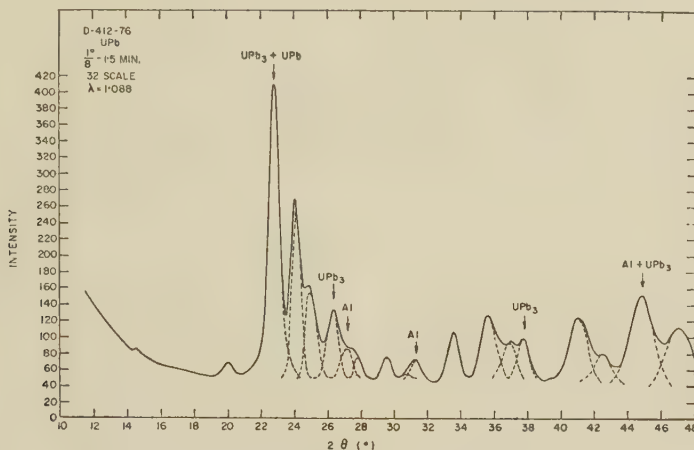


Fig. 4.—Neutron-Diffraction Pattern for Lead-Uranium Alloy, UPb.

problems. The specimens could be checked microstructurally to ascertain the number and types of phases present. Chemical sampling techniques were also greatly simplified.

## 1. ALLOY PREPARATION

Alloys for this study were made by an hydride technique already used for uranium-bismuth alloys.<sup>3</sup> The procedure was to place alternate layers of cleaned uranium chips and previously filtered lead lumps in an outgassed graphite crucible. The crucible was loaded into a vacuum furnace and heated to  $100^\circ\text{C}$ . The temperature was held at  $100^\circ\text{C}$ . until the pressure dropped below  $5\mu\text{ Hg}$ . Hydrogen gas was admitted and the crucible heated to  $250^\circ\text{C}$ . and held there until all the uranium had been converted to  $\text{UH}_3$ , which crumbles into a powder. By evacuating the furnace at  $250^\circ\text{C}$ ., the  $\text{UH}_3$  powder was decomposed to a fine uranium powder, which was more reactive and better packed than chips or bar stock. This mixture of uranium powder and lead was then heated to  $1220^\circ\text{C}$ . for 16 hr. The resulting ingot appeared to be homogeneous and was transferred to a thin-walled ( $\frac{1}{16}$  in.) aluminium can, sealed by means of a valve after evacuation.

## 2. EXPERIMENTAL PROCEDURE

The neutron-diffraction spectrometer and neutron monochromator used to obtain the pattern are described by Corliss *et al.*<sup>4</sup> The aluminium can containing the alloy was placed on the sample holder of the neutron spectrometer. A  $2 \times 2$ -in. collimated and monochromatic beam of neutrons ( $\lambda = 1.088 \text{ \AA}$ .) was directed on to the specimen, and the diffraction pattern shown in Fig. 4

examination of the fractured ingot did not show any uranium-rich sections. Therefore it was concluded that

TABLE I.—Neutron-Diffraction Data for  $\text{UPb}_3$ \*

$hkl$	Intensity † (Obs.)	$2\theta$	$d$ (Obs.)	$d$ (Calc.)
112	4.5	14.5	4.31	4.40
222	80	20.0	3.13	3.15
400	1440	22.75	2.76	2.76
141-330	816	24.0	2.61	{ 141-2.59 330-2.61
114	440	25.0	2.51	2.52
$\text{UPb}_3$	320	26.3	2.39	...
Al	144	27.15	2.35	...
242	88	27.65	2.27	2.25
143	104	29.60	2.13	2.135
105	16	30.5	2.07	2.09
Al	88	31.25	2.02	...
343	216	33.6	1.88	1.88
352	340	35.6	1.78	1.78
116-451	210	36.8	1.72	{ 116-1.73 451-1.71
$\text{UPb}_3$	230	37.8	1.68	...
170, 071, 550	456	41.0	1.555	1.555
552-406	192	42.5	1.50	{ 552-1.50 406-1.495
Al + $\text{UPb}_3$	81	44.8	1.425	...
237	480	47.0	1.362	1.362

\* Cell = body-centred tetragonal with  $c/a = 0.961$ ;  $c = 10.6 \text{ \AA}$ ;  $a = 11.04 \text{ \AA}$ ; number of atoms per cell = 48; density =  $13.7 \text{ g./c.c.}$

† Values calculated from spectrometer plot by multiplying the half width by the height for each diffraction line.

the alloy contained both UPb and  $\text{UPb}_3$ . One line ( $d = 2.76 \text{ \AA}$ ), attributed to  $\text{UPb}_3$ , was stronger than indicated by the  $\text{UPb}_3$  pattern. This line was probably due to a coincidence in the patterns of  $\text{UPb}_3$  and UPb.

Calculated line spacings of UPb were compared with Hull-Davey charts and found to correspond to a body-centred tetragonal structure having a  $c/a$  ratio of 0.96. According to the plane indices from the chart, the cell has the following dimensions:  $a = 11.04$ ,  $c = 10.60$  Å.,  $c/a = 0.961$ . Using these dimensions and an approximate density obtained by calculations assuming little change in atom size with compound formation, the number of atoms per unit cell was estimated to be  $50 \pm 5$ . This method of estimation has been used for the uranium-bismuth system, and the results agreed with those obtained by experimental density measurements. Since the cell has a body-centred symmetry and UPb is a bi-atom molecule, the actual number of atoms in the cell is a multiple of 4. Therefore, the number of atoms per cell is either 48 or 52. Judging from the immiscibility characteristics of the alloys, the number is most likely to be 48, which places the density of the compound at 13.7 g./c.c.

#### V.—THE LATTICE PARAMETER OF UPb<sub>3</sub>

Frost and Maskrey<sup>1</sup> give the lattice parameter and density of UPb<sub>3</sub> as 4.7834 Å. and 13.24 g./c.c., respectively. These values disagree with those reported in an earlier paper by the author<sup>2</sup> (4.791 Å and 12.98 g./c.c.). This discrepancy may be due to an oversight by Frost and Maskrey in converting kX units to Ångstroms, as that is exactly the ratio of the two values.

#### VI.—DISCUSSION

The evidence for liquid immiscibility would seem to be very strong, and the arguments of Frost and Maskrey are not entirely consistent. On the one hand, they admit difficulties in preparing alloys at high temperatures, but on the other hand their arguments favour complete miscibility at high temperatures, which would permit easy alloy preparation.

In the present work the definite, clean meniscus and the absence of a reaction layer rule out the possibility of incomplete alloying. It is improbable that the lead-rich phase should by coincidence always contain approximately 40% uranium and the uranium-rich phase only 1 or 2% lead.

Experiments have shown that alloys containing 50% uranium (slightly on the lead-rich side of UPb) segregate into two layers at high temperatures, one of which con-

sists of practically pure uranium. This can be explained only by a syntectic reaction. Gravitational separation cannot give this result.

The observation that homogeneous alloys can be made only at temperatures slightly lower than 1280° C. and cannot be produced at higher temperatures can be explained on the grounds of immiscibility but is not accounted for by the diagram of Frost and Maskrey.

Supercooling provides a very probable explanation of the thermal arrest observed by Frost and Maskrey at 1190° C. for a 15 at.-% lead alloy. At this composition, the reaction would be weak. As with peritectic reactions, it is probably necessary for the alloy to be at or near the syntectic composition for true reaction temperatures to be obtained.

There is no thermodynamic reason why a syntectic reaction cannot take place. Frost and Maskrey point out that the compound is below the maximum, but in fact, the compound composition is close to the lead-rich side of the reaction. The composition of the lead-rich liquid phase has not been well established, and it is possible that the true composition may be as high as 45% uranium, though it is definitely not above 53% uranium, the composition of UPb.

Even though the crystal structure of UPb has not been conclusively determined, the cell is large and complex, probably on account of the same forces as are responsible for the liquid immiscibility by which it dissociates.

The solubility of uranium in lead as determined by filtration at high temperatures gives values somewhat lower than that reported by Frost and Maskrey. The graphite filtration technique employed has been used on many alloy systems similar to the uranium-lead system, and by its means solubilities determined by settling and siphoning techniques have been satisfactorily checked.

#### ACKNOWLEDGEMENTS

The author wishes to thank the Physics Department at Brookhaven for the use of their neutron-diffraction equipment, as well as those persons already mentioned in his previous paper.<sup>2</sup>

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# THE LATTICE PARAMETERS OF THE ALPHA SOLID SOLUTIONS OF COPPER-ZINC-GERMANIUM AND COPPER-ZINC-GALLIUM ALLOYS\*

1764

By B. B. ARGENT,† B.Met., Ph.D., STUDENT MEMBER, and  
D. W. WAKEMAN,‡ B.Sc., Ph.D., MEMBER

## SYNOPSIS

It is shown that the expansion of the copper lattice caused by the solution of zinc and gallium, or zinc and germanium, may be expressed approximately as the sum of the expansions due to each of the solutes considered individually.

## I.—INTRODUCTION

A THERMODYNAMIC investigation of the  $\alpha$  solid-solution ranges of copper-zinc-germanium and copper-zinc-gallium alloys<sup>1</sup> having indicated that the heats of solution and entropies of solution showed certain anomalies which could not easily be explained, the present investigation was undertaken to find out whether similar anomalies existed in the lattice parameters of the alloys.

Accurate lattice-parameter measurements have been reported for the binary systems copper-zinc, copper-germanium, and copper-gallium<sup>2,3</sup> at the copper-rich ends, but no reference could be found to lattice-parameter measurements in the ternary systems.

## II.—EXPERIMENTAL

All the alloys were prepared from oxygen-free, high-conductivity copper (99.994%) supplied by Imperial Chemical Industries Ltd., Tadenac electrolytic zinc (99.994%), gallium (99.95%), and germanium (high-purity) supplied by Johnson, Matthey and Co., Ltd.

The alloys were made by melting the constituents in sealed clear silica tubes under an initial vacuum of 0.2  $\mu$  Hg. The tubes were shaken vigorously and quenched while the alloys were still liquid. The alloys were then homogenized for a week, at approximately 700° C.

Filings of the annealed alloys were swept with a magnet to remove iron particles, annealed at 400° C. for 18 hr. in evacuated Pyrex capsules, and air-cooled. The powders were made into rods with gum tragacanth and mounted in a 19-cm. cylindrical powder camera. Unfiltered manganese radiation was used to make the exposure, the wave-lengths assumed were: 2.1014<sub>9</sub> kX ( $K\alpha_1$ ); 2.0975<sub>1</sub> kX ( $K\alpha_2$ ); 1.9062<sub>0</sub> kX ( $K\beta_1$ ) (Siegbahn<sup>4</sup>).

All lattice parameters were corrected to 18° C. by using a linear expansion coefficient of  $17.5 \times 10^{-6}/^\circ\text{C}$ , a typical value for many copper-rich alloys. This made possible direct comparison with the work of Owen and Roberts<sup>2</sup> on the relevant binary systems. Values obtained by Hume-Rothery, Lewin, and Reynolds<sup>3</sup> for the binary systems were similarly corrected from 23° to 18° C.

## III.—RESULTS

The analyses of the alloys, the experimentally determined lattice parameters ( $a_{\text{expt.}}$ ), and the differences ( $a_{\text{expt.}} - a_{\text{calc.}}$ ) from lattice parameters calculated on the basis of the following assumed linear relationships, are tabulated in Tables I and II. By taking the lines of best fit to the initial portions of the lattice-parameter/atomic-

TABLE I.—Lattice-Parameter Values for Copper-Zinc-Gallium Alloys.

Cu, at.-%	Zn, at.-%	Ga, at.-%	$a$ (kX) $a_{\text{expt.}}$ (at 18° C.)	( $a_{\text{expt.}} - a_{\text{calc.}}$ )
74.4	20.7	5.0	3.6637	+0.0008
79.6	11.8	8.6	3.6546	—0.0012
81.6	6.3	12.1	3.6544	+0.0001
91.3	5.9	2.8	3.6244	—0.0030
91.3	2.6	6.1	3.6300	+0.0001
78.1	5.5	16.4	3.6626	—0.0021
85.8	6.5	7.7	3.6419	—0.0005
81.8	1.2	17.0	3.6577	+0.0001
85.3	0.4	14.3	3.6481	—0.0003
95.1	3.1	1.8	3.6190	+0.0002
72.4	24.8	2.8	3.6669	+0.0007
86.6	9.7	3.7	3.6355	—0.0022
80.8	17.7	1.5	3.6504	+0.0024
75.7	14.8	9.5	3.6671	+0.0027
70.3	25.1	4.6	3.6780	+0.0062
81.2	13.7	5.1	3.6512	+0.0013
83.6	13.6	2.8	3.6415	—0.0017
83.3	11.9	4.8	3.6448	—0.0005
81.0	3.1	15.9	3.6595	+0.0011
83.0	2.8	14.2	3.6548	+0.0018
85.2	2.5	12.3	3.6466	—0.0005
88.4	2.3	9.3	3.6393	+0.0010
89.7	6.2	4.1	3.6332	+0.0015
93.1	2.0	4.9	3.6250	—0.0003
95.7	1.6	2.7	3.6161	—0.0022
94.7	4.1	1.2	3.6195	+0.0002
87.0	5.7	7.3	3.6410	+0.0014
88.8	6.6	4.6	3.6350	+0.0011
84.2	6.7	9.1	3.6498	+0.0031

fraction curves for the three binary systems copper-zinc, copper-gallium, and copper-germanium and assuming an additive relationship for the lattice parameters of the ternary alloys, the following relationships were obtained:

$$a_{\text{Cu-Zn-Ga}} = 0.205x_{\text{Zn}} + 0.280x_{\text{Ga}} + 3.6075$$

$$a_{\text{Cu-Zn-Ge}} = 0.205x_{\text{Zn}} + 0.335x_{\text{Ge}} + 3.6075,$$

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where  $a_{\text{Cu-Zn-Ga}}$  and  $a_{\text{Cu-Zn-Ge}}$  are the lattice parameters of the copper-zinc-gallium and copper-zinc-germanium alloys, respectively, and  $x_{\text{Zn}}$ ,  $x_{\text{Ga}}$ ,  $x_{\text{Ge}}$  are the atomic fractions of the elements zinc, gallium, and germanium.

TABLE II.—*Lattice-Parameter Values for Copper-Zinc-Germanium Alloys.*

Cu, at.-%	Zn, at.-%	Ge, at.-%	$a$ (kX) expt. (at 18° C.)	( $a_{\text{expt.}} - a_{\text{calc.}}$ )
78.6	17.1	4.3	3.6592	+0.0022
83.1	9.8	7.1	3.6507	-0.0007
86.1	5.9	8.0	3.6467	+0.0003
88.7	2.3	9.0	3.6434	+0.0010
82.6	13.9	3.5	3.6491	+0.0014
85.9	8.6	5.5	3.6433	-0.0003
84.7	8.8	6.5	3.6481	+0.0008
90.7	1.7	7.6	3.6362	-0.0002
86.2	11.6	2.2	3.6405	+0.0018
90.1	6.8	3.1	3.6364	+0.0046
91.5	3.5	5.0	3.6320	+0.0016
92.7	1.7	5.6	3.6298	+0.0001
89.4	8.7	1.9	3.6329	+0.0012
92.6	4.6	2.8	3.6285	+0.0022
94.1	2.3	3.6	3.6268	+0.0025
94.7	0.9	4.4	3.6245	+0.0004
93.4	5.4	1.2	3.6233	+0.0007
94.3	3.2	2.3	3.6210	-0.0008
95.7	1.9	2.4	3.6191	-0.0003
96.5	0.6	2.9	3.6185	-0.0001

The lattice-parameter/composition curves for the binary systems deviate quite markedly from a linear relationship at concentrations greater than about 7–8 at.-% of the solute, and this probably accounts for some of the larger positive differences in col. 5 of Tables I and II. The few large negative differences may be due to excessive zinc loss on annealing the alloys. The differences in general indicate that no large deviations from additivity occur and thus give no supporting evidence for the anomalies shown in the thermodynamic work.

#### IV.—DISCUSSION

Raynor<sup>5</sup> has suggested that the lattice-spacing relationships of various elements in substitutional solid solution in copper, silver, and gold may be considered in terms of an atomic size-factor and a valency factor operating together. If it is assumed that the contribution to the change in the lattice spacing due to the difference between the valency of the solute and that of the solvent is the difference  $\Delta$  between the observed lattice spacing and that calculated from the atomic sizes of the components only, certain regularities are shown. In particular, where the solute is of the same period as the solvent, Raynor<sup>5</sup> showed that  $\Delta \propto (V_{\text{solute}} - V_{\text{solvent}})(e - 1)$ , where  $V$  denotes the valency and  $e$  the electron:atom ratio.

In the ternary systems we have investigated, the elements are of the same period. From the fact that the

phase diagrams of the systems zinc-gallium<sup>6,7</sup> and zinc-germanium<sup>8</sup> show simple eutectics with low mutual solubility, and from the thermodynamic data available on the system zinc-gallium,<sup>9</sup> we may conclude that the interaction between these pairs of solutes dissolved in copper is likely to be small. It is therefore probable that the effects on the copper lattice due to atomic size will be additive. In general, however, interactions between solutes are to be expected, so that additive relationships will not always occur. Hill and Axon<sup>10</sup> measured the lattice parameters of solutions of magnesium and silicon in aluminium and showed that there existed an unambiguous negative deviation from a linear relationship. This is a case in which interaction between the solutes would clearly be expected.

The compositions we have studied cover fairly thoroughly the primary solid-solution ranges of the two systems. The fact that the lattice parameters are approximately additive, indicates that the effects of the valency factors may also be additive.

A few lattice parameters measured by Stirling and Raynor<sup>11</sup> for the primary solid-solution range of aluminium and indium in copper also indicate an additivity relationship. These results, taken together with those reported in the present paper, tend to support the common assumption of additivity of size and electronic effects in discussions of similar systems.

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# A NOTE ON THE BRITTLE INTERGRANULAR FRACTURE OF BETA-BRASS\*

1765

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(Communication from The British Non-Ferrous Metals Research Association)

## SYNOPSIS

Stress concentrations at grain boundaries, in conjunction with a rapid rate of straining, are shown to be essential factors in causing intercrystalline failure at high temperatures in ordered  $\beta$ -brass.

## I.—INTRODUCTION

It has been reported by several investigators<sup>1-4</sup> that  $\beta$ -brasses containing aluminium are subject to brittle intercrystalline fracture in various ranges of strain rate and temperature. Perryman<sup>4</sup> has shown that under impact loading conditions an intercrystalline brittle range occurs from about 400° to 500° C. Similar failures were observed at room temperature under sustained loads, the time to fracture varying from 1 to 500 hr. Perryman also showed, from X-ray back-reflection photographs of the fracture facets, that the grain-boundary surfaces lying at an angle to the applied stress, and hence in a position to undergo a shearing motion, showed a much deeper distorted layer than those which were perpendicular to the applied stress. Perryman concluded that this evidence was in favour of a mechanism, first put forward by Zener,<sup>5</sup> by which intercrystalline failure is caused by the high local stresses at the corners between relaxed and unrelaxed boundaries, and that a brittle,  $\gamma$ -phase precipitate at the grain boundaries is not essential in causing brittle intercrystalline fracture.

To investigate this aspect further, it seemed desirable to attempt to produce intercrystalline fracture in specimens having no grain corners, and a few simple tests have been performed on bicrystals containing one plane grain boundary.

## II.—EXPERIMENTAL PROCEDURE

An alloy containing copper 58.6, zinc 38.4, and aluminium 3%, was made from cathode copper (99.99%), electrolytic zinc (99.99%), and super-purity (99.99%) aluminium. On metallographic examination the alloy appeared to be single-phase  $\beta$ .

Bicrystal bars of this material were grown by progressive solidification from the liquid, in graphite moulds under an argon atmosphere. Cylinders 1 in. long and 0.25 in. in dia. were machined mechanically from the bicrystal bars in such a manner that the grain boundary was in the centre of the bar and perpendicular to the axis of the cylinder. An electrolytic lathe similar to that described by Farmer and Glaysher<sup>6</sup> was used to

turn down the centre gauge-length of the specimen and remove the cold-worked surface layers, so that the surface gave sharp back-reflection Laue spots. The surface was then electropolished while still in the lathe.

In addition to these, bicrystals specimens were prepared having two grains across the cross-section to produce grain corners. These were obtained in a similar fashion to the bicrystals but, by employing high rates of heat extraction, several nuclei were encouraged to form in the melt.

Finally, some polycrystalline specimens were machined from the original cast slab. These had about ten grains in a cross-section.

All tests were performed at 400° C. in air. Impact tensile tests were carried out simply by dropping a weight into a scale pan rigidly affixed to the bottom of the specimen, stress-rupture tests by applying a dead load, and normal tensile tests by means of a Hounsfield tensometer.

## III.—EXPERIMENTAL RESULTS

### 1. TENSILE TESTS

All specimens tested gave ductile fractures. The fine-grained specimens had ultimate tensile strengths of 9000 lb./in.<sup>2</sup> and extensions approaching 100%. Examination of the specimens showed that there had been considerable deformation in the grain-boundary regions, leading to recrystallization in many cases, as illustrated in Fig. 1 (Plate LXVI). The coarse-grained specimens were equally ductile in regions away from the grain boundaries, the grain-boundary regions being less distorted and standing proud of the rest of the specimens. The bicrystal specimens deformed mainly in one grain only, giving a chisel-shaped fracture.

### 2. STRESS-RUPTURE TESTS

These were carried out on the fine-grained and coarse-grained specimens only. Table I shows the results obtained.

All the fractures were ductile, with evidence of sliding along grain boundaries. Thus, in Fig. 2 (Plate LXVI)

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sliding on one grain boundary has led to a crack starting on the top surface where the grain boundary meets a corner, but the crack has failed to penetrate into the grain just below it. The fine-grained specimens numbered 4, 5, and 6 all completely recrystallized during the test, while specimens 7 and 8 had not recrystallized

TABLE I.—*Stress-Rupture Tests on Polycrystalline  $\beta$ -Brass Containing Aluminium at 400° C.*

	Specimen No.	Stress, lb./in. <sup>2</sup>	Time to Fracture, hr.
Coarse-grained	1	5000	3
	2	3400	4
	3	1700	6
Fine-grained	4	2200	1
	5	1400	5
	6	730	103
	7	360	Unfractured after 250 hr.
	8	180	

but showed considerable grain-boundary sliding and migration.

### 3. IMPACT TENSILE TESTS

Both coarse- and fine-grained specimens gave brittle intercrystalline fracture under impact loading conditions, as previously reported.<sup>4</sup> Fig. 3 (Plate LXVI) shows a coarse-grained specimen which on fracturing along the grain boundaries has completely ejected a whole grain. Three bicrystals were tested: (i) with a plane grain boundary perpendicular to the applied stress, (ii) with a slightly curved boundary, and (iii) with a boundary consisting of three facets, the central facet being perpendicular to the applied stress with two side facets inclined at an angle of approximately 10°. Specimens (i) and (ii) behaved in a precisely similar fashion to that observed in the tensile tests, giving a ductile chisel-type fracture (Fig. 4, Plate LXVI). Specimen (iii), however, fractured along the grain boundary without any evidence of plastic deformation (Fig. 5, Plate LXVI).

### IV.—DISCUSSION

It is concluded that to cause brittle fracture in aluminium-containing  $\beta$ -brass it is necessary for the grain configuration to be such that stress concentrations are produced at the corner where relaxed and unrelaxed grain boundaries meet. That grain boundaries can relax by a shear deformation at the high speeds demanded in an impact test is illustrated in Fig. 6 (Plate LXVI), where brittle fracture has occurred along a grain boundary, and a large step is visible at the grain boundary to the right of the fracture. There would seem at first sight to be a contradiction between the ductile failure at low strain rates at 400° C. and the intercrystalline failure at room temperature reported by Perryman,<sup>4</sup> but it appears that two different processes are in control at these two temperatures. At low temperatures the controlling factor is the slow rate of shearing at the grain boundaries, a long time being required to give sufficient movement to provide the necessary stress concentration; while at elevated temperatures the grain boundaries slide very rapidly, but the stress concentration produced can be dissipated by grain-boundary migration and recrystallization.

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# THE BEHAVIOUR OF FRACTURED COPPER FATIGUE SPECIMENS ON ANNEALING \*

1766

By D. S. KEMSLEY,† M.Sc., B.A., F.M.T.C.

## SYNOPSIS

Fractured rotating-cantilever specimens covering a considerable portion of the  $S/N$  diagram have been annealed at constant temperature and also at constant heating rate. Hardness, metallographic, and X-ray-diffraction observations have been made at certain stages during annealing. In low-stress ( $\pm 11,000$ – $15,000$  lb./in.<sup>2</sup>) specimens, deformation markings (striations) revealed by etching disappear over a wide temperature range, while at the same time there is a drop in hardness which is rapid at first and then slows down; recrystallization does not occur. On the other hand, high-stress ( $\pm 25,000$  lb./in.<sup>2</sup>) specimens, in which etching does not reveal striations, recrystallize over a narrow range of temperature, with an associated rapid drop in hardness. This behaviour is comparable with that of a tensile specimen similarly annealed. These results suggest an explanation of the reported failure of repeated annealing during interrupted low-stress fatigue tests on copper and 70 : 30 brass to increase fatigue life, and also emphasize the difference between the modes of deformation occurring under low and under high cyclic stress.

## I.—INTRODUCTION

RECENTLY, characteristic deformation markings (striations) consisting of slip packets have been developed in fractured copper fatigue specimens by etching.<sup>1</sup> Such markings are known<sup>2</sup> to be most numerous under low-stress conditions, and to be virtually absent from high-stress specimens. The conclusion was reached that localized deformation most truly characteristic of cyclic stress occurs predominantly in low-stress specimens, and that as the stress increases, deformation becomes less localized and more like that produced by unidirectional stress. It was therefore considered that the reactions to annealing of low- and high-stress specimens would be of interest, and the present paper contains results obtained by optical microscopy, X-ray-diffraction examination, and hardness tests.

During recent work on the release of stored energy from fractured low-stress copper fatigue specimens, Clarebrough *et al.*<sup>3</sup> observed that recrystallization had not occurred on annealing to 600° C., even though all measurable stored energy had been released below that temperature. This indicated that some mechanism other than normal recrystallization was here responsible for the release of stored energy. Furthermore, heating such specimens to 600° C. did not reduce the hardness to the level obtaining before testing. It was also known that periodic annealing during testing had failed to increase the fatigue lives of low-stress steel,<sup>4</sup> brass,<sup>5</sup> and copper<sup>6-9</sup> specimens, the annealing temperature employed in the last case being 600° C.† The phenomenon has been interpreted as being due to the presence of incipient cracks in the early stages, but Clarebrough's results suggested that this was possibly not the correct explanation, and that some "damage" other than cracking persisted in such specimens to much higher temperatures than was previously believed. These facts added further point to the investigation.

While the present paper was being prepared, Wood<sup>10</sup> published an account of the annealing of a low-stress copper fatigue specimen, and contrasted its behaviour with that of a tensile specimen. The work now described extends Wood's results by employing metallographic observations and also high-stress fatigue specimens.

## II.—EXPERIMENTAL CONDITIONS

### 1. SPECIMENS

Six copper rotating-cantilever fatigue specimens were prepared from the same material and to the same design as in previous investigations.<sup>1, 2, 11, 12</sup> A tensile specimen was also prepared from this material. Four of the fatigue specimens and the tensile specimen were polished mechanically, and then electrolytically in orthophosphoric acid solution. Finally, all specimens were vacuum-annealed at 600° C. for 1 hr. No further surface preparation of the electropolished specimens was necessary before testing, as the vacuum present during annealing was sufficient to retain the highly polished surfaces. The fatigue specimens were cycled to fracture at stresses ranging from  $\pm 11,000$  ("low stress") to  $\pm 25,000$  lb./in.<sup>2</sup> ("high stress") at a frequency of 6000 c./m., according to the schedule given in Table I; the number of cycles to reach full load was approximately 2500 and 3500 at low and high stress, respectively. The tensile specimen was elongated 10%, i.e. to a hardness of 72 D.P.N. All specimens were subsequently examined, some of them after further annealing treatment, as indicated in Table I.

The same half of each specimen was used for examination in the as-fractured and annealed conditions. The amount of surface rumpling produced by low and high stresses was observed on the sectioned halves of specimens Nos. 3 and 6. Details of the procedure adopted in preparing the longitudinal microsections, the etchant

\* Manuscript received 24 July 1956.

† Department of Supply, Aeronautical Research Laboratories, Fishermen's Bend, Melbourne, Australia.

‡ This negative result has also been obtained for copper in the Aeronautical Research Laboratories, the annealing temperature being again 600° C.

employed to develop fatigue deformation markings after electrolytic polishing, and the manner in which hardness

TABLE I.—*Experimental Conditions.*

Specimen No.	Type of Stress	Finish	Stress, $\pm$ lb./in. <sup>2</sup>	Life, cycles	Examination	
					As-Fractured Condition	Annealed Condition
1	Cyclic	Machined	12,000	6,964,000	A	C
2			20,000	145,800	A	C
3		Electro-polished	11,000	31,294,000	A, B	D
4			15,000	1,466,000	B	D
5			20,000	180,000	B	D
6			25,000	35,800	A, B	D
7	Tensile	Electro-polished	...	(10% tensile elongation)	B	D

## KEY

A = hardness, X-ray-diffraction, and metallographic examination of longitudinal section.

B = hardness, X-ray-diffraction, and metallographic examination of specimen surface.

C = same as A, after 1-hr. anneal at 600° C.

D = same as B, generally at each 50° C. during heating at 6° C./min.

and X-ray tests were carried out have been discussed previously.<sup>2</sup>

## 2. ANNEALING SCHEDULES

The two conditions of annealing followed, on the one hand, the treatment adopted by Thompson *et al.*<sup>7</sup> and also recently by Wood<sup>10</sup> (constant temperature: 600° C. for 1 hr.), and on the other hand that of Clarebrough *et al.*<sup>3</sup> (constant heating rate: 6° C./min.). All annealing was carried out in vacuum. In the constant-heating-rate experiments, heating was normally interrupted each 50° C. for hardness tests and X-ray and metallographic examination. At each interruption, the specimen was rapidly cooled, electropolished, etched, and examined. Annealing was resumed by reheating rapidly to the temperature of withdrawal and then at 6° C./min. to the next selected temperature. This process was continued up to 960° C.

## III.—RESULTS

## 1. HARDNESS/TEMPERATURE RELATIONSHIPS

In all the fatigue specimens, the initial annealed hardness of approximately 35 D.P.N. had increased to approximately 70 D.P.N. at fracture, irrespective of the magnitude of the cyclic stress. This agrees with previous results.<sup>11</sup>

Annealing at 600° C. for 1 hr. reduced the hardness of a low-stress specimen (No. 1) to 44.5 D.P.N., and that of a high-stress specimen (No. 2) to 35.1 D.P.N., indicating complete softening in the latter case but not in the former. The effect on hardness of heating the remaining specimens at 6° C./min. is shown in Fig. 1. It should be noted that the curves for individual specimens have been displaced vertically in this figure. Specimens stressed in the range  $\pm 11,000$ – $\pm 20,000$  lb./in.<sup>2</sup> softened in two stages, while the high-stress specimen and the tensile specimen displayed no such break in the hardness/temperature relationship.

Fig. 1 also shows that, as cyclic stress increases, the

temperature at which softening begins is lower, the temperature range of the first stage of softening is generally wider, and the hardness drop in this stage is greater. Furthermore, the second stage becomes less definite, and is absent in the high-stress specimen (curve 4). Finally, there is a general similarity between the high-stress fatigue specimen and the tensile specimen, although the hardness decreases more rapidly in the latter.

## 2. OPTICAL MICROSCOPIC EXAMINATION

It was found that surface slip bands adjacent to the fracture became more numerous as the cyclic stress increased (Figs. 2–5, Plate LXVII), and that surface roughening became more marked (Figs. 10 and 11, Plate LXVIII).

Structural changes produced in low- and high-stress specimens on annealing at 600° C. for 1 hr. are illustrated in Figs. 6–9 (Plate LXVII). Fig. 6 shows a typical area in the low-stress specimen, exhibiting a fatigue crack, and, in particular, deformation markings (striations). Fig. 7 shows the same area after annealing, followed by repolishing on 35- and 15- $\mu$  pads plus electrolytic polishing. While this treatment must of necessity alter details in the microstructure, it should be noted that the deformation markings have been removed by the annealing treatment, and that recrystallization, if it has occurred at all, has certainly been very restricted. On the other hand, striations were virtually absent from the high-stress specimen at fracture (Fig. 8), and on heating complete recrystallization resulted (Fig. 9). This dependence of annealing behaviour on stress level has been verified in other machined specimens covering several grain-sizes; furthermore, the grain-sizes of specimens employed for the constant-heating-rate experiments were all closely similar, and again confirmation of the two types of annealing behaviour was obtained. Thus, although the grain-sizes in Figs. 6 and 8 differ, this variation would appear to have little influence on the end results.

Micro-examination of those specimens heated at constant rate yielded more detailed information concerning the removal of striations and of recrystallization in low- and high-stress specimens, respectively. Striations, which were clearly visible in the specimens stressed at  $\pm 11,000$  and at  $\pm 15,000$  lb./in.<sup>2</sup>, began to decrease in intensity at 350° C., and had disappeared entirely at 800° C. This was the only change observed in the former specimen, but in the latter recrystallization, which set in at 500° C., occurred in a few isolated regions. On the other hand, the remaining two fatigue specimens stressed at  $\pm 20,000$  and at  $\pm 25,000$  lb./in.<sup>2</sup> recrystallized completely, the process occurring over the temperature range 500°–800° C. in the former and 450°–700° C. in the latter case.

Slip bands present on the surface of the tensile specimen after 10% elongation were finer and more wavy than those developed in the fatigue specimens. The surface of this specimen was rumpled. On heating at 6° C./min., recrystallization began at 450° C. and was complete at 500° C.

Grain growth was observed in all specimens between 900° and 960° C.; it was most marked in the low-stress



fatigue specimen, and least noticeable in the high-stress fatigue and the tensile specimens.

### 3. X-RAY DIFFRACTION PATTERNS

In all cases, X-ray patterns of the fatigue specimens before testing consisted of discrete sharp spots characteristic of completely annealed material. Fracture under low cyclic stress produced slight arcing of the spots (Fig. 12, Plate LXVIII) which increased with increasing stress, finally resulting in complete rings at high stress (Figs. 13-15, Plate LXVIII). The pattern obtained from

### IV.—DISCUSSION

Certain well-known distinctions exist between initially annealed materials when fractured under low and high cyclic stresses. The more important are:

- (1) The number of cycles of stress required to produce fracture is large at low stress, and relatively small at high stress.
- (2) Surface slip bands are least numerous at low stress, and increase in number as cyclic stress increases.
- (3) Surface roughening is very small at low stress, but is pronounced at high stress.

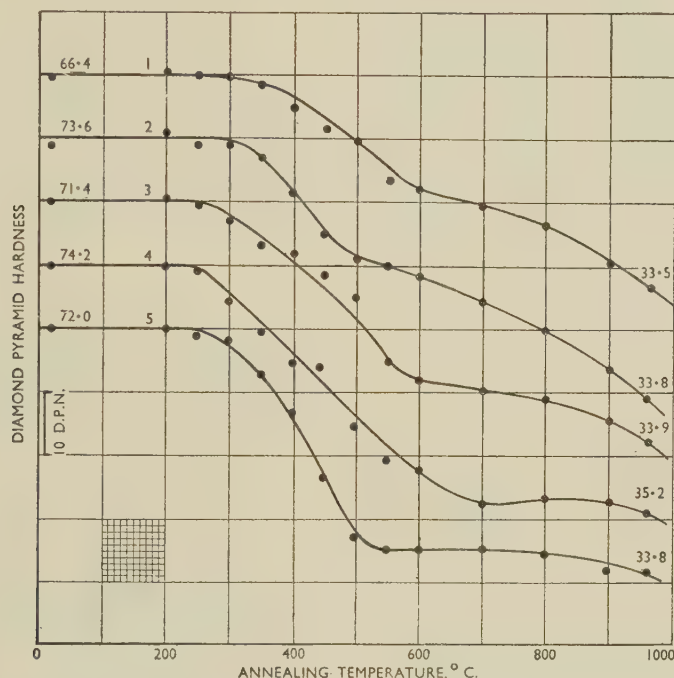


FIG. 1.—Hardness/Annealing-Temperature Relationships for Specimens Heated at 6° C./Min.

Note that the curves are displaced vertically.

- Curve 1. Fatigue specimen (No. 3), fractured at  $\pm 11,000$  lb./in.<sup>2</sup>.
- Curve 2. Fatigue specimen (No. 4), fractured at  $\pm 15,000$  lb./in.<sup>2</sup>.
- Curve 3. Fatigue specimen (No. 5), fractured at  $\pm 20,000$  lb./in.<sup>2</sup>.
- Curve 4. Fatigue specimen (No. 6), fractured at  $\pm 25,000$  lb./in.<sup>2</sup>.
- Curve 5. Tensile specimen (No. 7), elongated 10%.

the tensile specimen after deformation also consisted of complete rings.

Annealing under constant-heating-rate conditions produced the following effects in these various X-ray patterns. With the low-stress specimen, the initial small amount of arcing diminished progressively with increasing temperature, but complete sharpening of the spots did not occur until a temperature of 960° C. was reached. The behaviour of the high-stress and the tensile specimens was, however, conventional, in that diffraction rings indicative of the cold-worked condition were gradually replaced on annealing by sharp spots from the new grains which were forming. Spots first appeared at 350° C. and the process was complete at 700° C. in both specimens. The two specimens tested at intermediate stress levels behaved on annealing in a similar manner to the low-stress specimen, completely sharp spots not being obtained until temperatures of 900°-960° C. were reached.

- (4) The X-ray-diffraction pattern from a fractured low-stress specimen is spotty, while that from a high-stress specimen consists of complete rings.

An additional difference has been noted for the particular case of the fatigue of annealed copper, in that deformation markings (striations) consisting of slip packets can be revealed both on the surface and in the interior of low-stress specimens by suitable etching, whereas such markings are virtually absent in the high-stress case.<sup>2</sup>

The work under discussion provides further grounds for discriminating between the effects of low and high cyclic stresses, since it indicates a completely different reaction to annealing in low-stress and high-stress specimens. The most obvious difference is that a low-stress specimen does not recrystallize, whereas a high-stress one does so. Furthermore, in the low-stress case, hardness falls off slowly over a wide temperature range

as a two-stage process associated with gradual disappearance of striations and sharpening of X-ray-diffraction spots. On the other hand, the high-stress case tends to follow the normal recrystallization behaviour of copper cold-worked by unidirectional stress, viz. recrystallization over a relatively narrow temperature range in one stage. These observations are in agreement with Wood's conclusions<sup>10</sup> that deformation was "laminar" in low-stress fatigue and "turbulent" in tension. In addition, the fact demonstrated by Clarebrough *et al.*<sup>3</sup> that a low-stress copper fatigue specimen had not recrystallized on heating to 600° C. has been confirmed.

An explanation of the formation of striations in low-stress specimens has been given previously.<sup>2</sup> It was considered that parallel lines of edge dislocations of opposite sign formed on adjacent slip planes and acted as "cores" around which subsequent dislocations wrapped themselves. This model provides one possible explanation of the present results obtained from low-stress specimens. Louat, to whom the original model is due,<sup>13</sup> has suggested<sup>14</sup> that the first stage in the hardness/temperature relationship of such specimens may be associated with the elimination of the dislocation loops surrounding cores, the second stage involving dispersal of the cores themselves. He suggests that the energy associated with the former process should be large, while that in the latter should be small.

These concepts provide a basis for an explanation of two experimental observations. First, the life of low-stress copper fatigue specimens is unaffected by periodic annealing at 600° C.<sup>6-9</sup>; since it now seems unlikely that incipient cracks are present at a sufficiently early stage in the life to produce this effect,<sup>12</sup> the deformation still remaining at 600° C., i.e. corresponding to a hardness of approximately 45 D.P.N., represents an important part of the total deformation. In terms of Louat's suggestion, cores could still exist at this temperature and therefore periodic annealing at temperatures approaching 900° C. would be necessary to obtain any substantial increase in fatigue life at low stress. A similar explanation would account for the lack of increase in fatigue life of 70:30 brass periodically annealed at 400° C.<sup>5</sup>

The second observation is that energy is gradually released up to approximately 450° C. from low-stress copper fatigue specimens, no further energy in measurable amount being released up to 600° C.<sup>3</sup> This is to be expected if, in fact, the energy associated with the removal of dislocation loops around cores is considerably greater than that involved in the dispersal of the cores themselves.

A theoretical interpretation of the behaviour of the high-stress and tensile specimens must await a satisfactory theoretical concept of the mechanism of recrystallization.<sup>15</sup>

#### ACKNOWLEDGEMENTS

This work forms part of the research programme on fatigue at the Aeronautical Research Laboratories, and the author would like to thank Dr. A. K. Head, Dr. N. Louat, and Dr. H. L. Wain for helpful discussions. Acknowledgement is made to the Chief Scientist, Department of Supply, Australia, for permission to publish the paper.

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## 1767 CRACK PATHS IN FATIGUED COPPER \*

By D. S. KEMSLEY,† M.Sc., B.A., F.M.T.C.

#### SYNOPSIS

Cracks in fractured copper fatigue specimens were found to be intercrystalline in specimens tested at high stress ( $\pm 25,000$  lb./in.<sup>2</sup>) and transcrystalline in those fractured under low stress ( $\pm 15,000$  lb./in.<sup>2</sup>). Both types of crack were produced at intermediate stresses. All tests were made in a rotating-cantilever machine at 6000 c./m.

#### I.—EXPERIMENTAL

BOTH transcrystalline and intercrystalline fatigue cracks have been observed in copper fatigue specimens tested in air,<sup>1</sup> but the factors governing the formation of the two types have not been discussed.

A study of the problem has now been made on rotating-cantilever fatigue specimens, prepared as described

earlier<sup>2</sup> from high-conductivity copper (99.95%). Each specimen was electropolished and annealed at 600° C. for 30 min. before testing to fracture (see Table I).

Diametric longitudinal sections were prepared from one half of each fractured specimen as before,<sup>2</sup> and etched in dilute acid ferric chloride solution for 4 sec. The paths of all cracks within 3 mm. of the main fracture were examined by the optical microscope and classified as in

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Table I. No decision was possible as to the paths of the main cracks, and these have not been included in the table, but there is no reason to suspect that they would differ from those examined. Transcrystalline cracks

TABLE I.—Test Conditions and Crack Paths  
(Longitudinal Sections Only).

Finish: electropolished. Frequency: 6000 c./m.

Specimen No.	Stress, lb./in. <sup>2</sup> *	Life, Cycles	No. of Cracks	Crack Path		
				Transcrystalline		Inter-crystalline
				Along Striations	Along Twin Boundary	
1	±11,000	$3.1 \times 10^7$	Nil	Nil	Nil	Nil
2	±15,000	$1.5 \times 10^6$	18	10	8	Nil
3	±20,000	$1.8 \times 10^5$	8	3	4	1
4	±25,000	$3.6 \times 10^4$	5	Nil	Nil	5

\* Specimens tested at ±11,000–±15,000 lb./in.<sup>2</sup> and ±25,000 lb./in.<sup>2</sup> are referred to in the text as “low-stress” and “high-stress” specimens, respectively.

were subdivided into those running along deformation markings (“striations”) revealed by etching,<sup>2,3</sup> and those situated on annealing-twin boundaries. The various types of crack are illustrated in Figs. 1–3 (Plate LXVIII).

## II.—DISCUSSION

From Table I, it appears that cracks were transcrystalline in the low-stress specimen (±15,000 lb./in.<sup>2</sup>), and intercrystalline in the high-stress specimen (±25,000 lb./in.<sup>2</sup>), while a mixture of the two types was present in the specimen tested at intermediate stress (±20,000 lb./in.<sup>2</sup>). Examination of the repolished surfaces of the remaining halves of the specimens gave similar results to the sections. Although a distinction has been drawn between the two types of transcrystalline crack, this may not in fact be valid, since annealing-twin boundaries appear to be preferred sites for formation of striations.<sup>2,4</sup> These results have been confirmed on specimens with a finely turned finish, tested under similar conditions.

As regards the observed dependence of crack path on stress level, it has been suggested<sup>2</sup> that low cyclic stresses favour the multiplication of slip lines into packets, but that high cyclic stresses do not allow this multiplication process to occur so readily. Consequently, in some way as yet unknown, the development, in low-stress specimens, of localized slip packets may lead to complete fracture in certain of these packets. This explanation cannot apply, however, to high-stress specimens, but the marked surface rumpling which occurs seems to result in valleys at grain boundaries (see Fig. 3); these, acting as stress concentrators, may be the cause of intercrystalline failure.

The present observations may provide an explanation of the effect of grain-size on fatigue life. At low stress, an increase in grain-size would result in an increase in the length of the slip packets produced and therefore of resultant cracks; it would thus be expected that fatigue life would be reduced. Although no results appear to be available for copper, the lives under low stresses of a variety of other metals are in fact significantly reduced by increase in grain-size.<sup>5–10</sup> At high stress, a larger grain-size would mean that there were fewer grain boundaries, and therefore an increase in fatigue life would be expected. No reference in the literature to the effects of grain-size on fatigue life at high stress has, however, been noted.

## ACKNOWLEDGEMENT

Acknowledgement is made to the Chief Scientist, Department of Supply, Australia, for permission to publish this paper.

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# 1768 A NOTE ON THE EFFECT OF ANTIMONY ON HOLE FORMATION DURING THE DIFFUSION OF ZINC FROM BRASS *IN VACUO*\*

By L. M. T. HOPKIN,† Ph.D., A.R.S.M., A.I.M., MEMBER  
(Communication from the National Physical Laboratory)

## SYNOPSIS

It is shown that during the diffusion of zinc from brass heated *in vacuo* the presence of antimony increases the formation of the holes, associated with the Kirkendall effect, which are attributable to the precipitation of excess vacancies. This observation provides additional support for the author's previous suggestion (*J. Inst. Metals*, 1955-56, **84**, 102) that the severe intergranular brittleness encountered in copper-antimony alloys during plastic deformation at elevated temperatures arises from the effect of antimony in promoting the precipitation of excess vacancies produced by the deformation.

## I.—INTRODUCTION

In a previous paper,<sup>1</sup> it was shown that the addition of between 1 and 2% of antimony to copper produced severe intergranular embrittlement in impact and tensile tests at elevated temperatures. Not only were the fractures intergranular, but extensive intergranular fissures, which appeared to be formed by the linking together of isolated holes, occurred well removed from the fracture. These results were consistent with the suggestion of Greenwood *et al.*<sup>2</sup> that intergranular cracking in creep is due to the precipitation at grain boundaries of excess vacancies produced by the plastic deformation. At the present time, however, the evidence supporting Greenwood's hypothesis is not extensive, and some schools of thought believe that other mechanisms are responsible for cracking during deformation at elevated temperatures. It is therefore desirable that the concept of the precipitation of vacancies at grain boundaries as the cause of intergranular embrittlement should be further examined.

An excess of vacancies can be produced not only by plastic deformation but also by intermetallic diffusion in couples where the unequal rates of diffusion of the components give rise to the Kirkendall effect. This excess of vacancies occurs regardless of whether diffusion takes place interstitially or via a vacancy mechanism. If diffusion is primarily interstitial, vacancies are generated in the diffusion zone as atoms leave their lattice sites and enter the interstices; if diffusion occurs by vacancy-atom exchange, vacancies are pumped into those regions which atoms are leaving. In either case, the component of the couple with the faster rate of diffusion becomes supersaturated with vacancies in the diffusion zone, and it is now generally believed that when the degree of this supersaturation is sufficiently high there takes place nucleation of the holes characteristically associated with the Kirkendall effect (see Le Claire<sup>3</sup>). If, then, it could be shown that antimony increases hole formation during diffusion, as well as the intergranular cracking during plastic deformation at

elevated temperatures observed previously,<sup>1</sup> there would be stronger evidence from which to conclude that cracking during deformation results from precipitation of vacancies. It is the purpose of this note to describe experiments designed with this objective in view.

Holes associated with the Kirkendall effect can readily be obtained by diffusing zinc out of  $\alpha$ -brass at a suitable temperature *in vacuo*.<sup>4, 5</sup> Under these conditions zinc atoms diffuse to the surface, where they are removed into the vacuum more quickly than the copper atoms are diffusing in the opposite direction. In consequence, an excess of vacancies is produced which gives rise to the formation of holes. If the difference between the rates of diffusion of copper and zinc were entirely compensated by hole formation, the only dimensional change observable for thin sheets should be a reduction in thickness. Balluffi and Seigle,<sup>6</sup> however, have demonstrated that for foil about 0.003 cm. thick there is also a contraction in length, a small proportion of which is dependent on grain-size. They show that this contraction is not due to surface-energy phenomena and attribute the effect to the absorption of vacancies: (1) at grain boundaries, without the formation of holes, so that contiguous grains approach each other, thus producing a contraction in the length of a sheet, and (2) at dislocations, causing their climb at right angles to the slip plane and a contraction parallel to the slip plane. In a face-centred cubic crystal the shrinkage should tend to be isotropic, because of the multiplicity of slip planes. The effect of the former process is small compared with the latter. Balluffi and Seigle also found that extensive cracking and the formation of holes at grain boundaries occurred only in the sheets over 0.015 cm. thick, an effect attributed to internal stresses developed in these sheets during diffusion. Loss of zinc causes a contraction, so that as zinc is removed from the surface of a sheet the outer layers come to be in tension while the interior layers are in compression. These stresses are greater, the thicker the material. The tensile stresses aid the formation of holes, since nucleation of a hole is accompanied by some stress-relief.

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Since the present investigation was begun, the influence of minor additions of several elements, including antimony, on the diffusion of zinc from brass *in vacuo* has been reported by Accary.<sup>7</sup> He found that the rate of loss of zinc from 70 : 30 brass increased with antimony content up to 0.06%, the maximum concentration studied. Metallographic examination of the surface of the specimens, roughened by the removal of zinc, showed that there was more pitting, particularly at grain boundaries, in antimony-bearing than in antimony-free specimens, and Accary concludes that antimony provokes intense grain-boundary diffusion of zinc. No sections of the specimens were examined, however, and it is not clear whether the pitting observed was more than a surface phenomenon unassociated with the precipitation of vacancies.

In the present experiments the effect of antimony in  $\alpha$ -brass on the formation of holes within the specimens during diffusion of the zinc was examined under two conditions: (1) in the presence of internal stresses, i.e. in thick specimens, and (2) where the internal stresses are a minimum and no cracking or hole formation occurs at grain boundaries, i.e. in very thin sheets.

## II.—MATERIALS

McLean and Northcott<sup>8</sup> have shown that 0.2% antimony is the maximum amount that can be tolerated in 70 : 30 brass from the point of view of fabrication. This concentration of antimony forms a solid solution in brass. Accordingly, the alloys tested contained (a) 25% zinc and (b) 27.6% zinc and 0.19% antimony. These materials were cold rolled from 1-in.-dia. ingots to  $\frac{5}{8}$ -in.-dia. rod, annealed, machined to  $\frac{3}{8}$ -in.-dia. rod and cold swaged to  $\frac{1}{4}$ -in.-dia. rod (final reduction 55%). Some of the  $\frac{3}{8}$ -in.-dia. rod was cold rolled to foil 0.003 cm. thick with one intermediate anneal in an evacuated silica capsule. The  $\frac{1}{4}$ -in.-dia. rod and the 0.003-cm.-thick foil were finally annealed for 24 hr. at 800° C. in an evacuated silica capsule to stabilize the grain-size. Finally, zinc was distilled off the specimens in a vacuum furnace.

## III.—RESULTS

### 1. ROD SPECIMENS

Figs. 1 (a) and (b) and 2 (a) and (b) (Plate LXIX) show the marked effect of the antimony addition after heating the specimens for 1 hr. at 800° C. The specimens had retained their yellow colour during this treatment, except for the surface layer containing holes. In the antimony-free brass the intergranular cracking is slight, and there is little tendency for the holes to form at grain boundaries (Figs. 1(a) and (b)). In the antimony-bearing brass, intergranular cracking is so extensive that some of the grains have fallen out (Fig. 2 (a)). In Fig. 2 (b), which shows the same specimen as that in Fig. 2 (a) but at a higher magnification, it is quite clear that the extensive cracking results from the linking together of isolated holes. Comparison of Fig. 1 (b) and Fig. 2 (b) shows that the holes in the antimony-bearing material are smaller than those in the antimony-free material.

The marked effect of the presence of antimony was not

due to the slightly higher zinc content of the antimony-bearing alloy, since a test on an antimony-free brass containing 29.5% zinc produced the same results as for the 25% zinc brass. Similarly, the absence of any effect in an alloy containing 0.2% antimony without zinc showed that the severe cracking in the antimony-bearing brass was not due to the presence of antimony alone.

### 2. FOIL SPECIMENS

The results for the foil specimens are given in Table I. In the first set of results the specimens were slowly heated to 800° C. and held at this temperature for 1 hr.

TABLE I.—Diffusion of Zinc from Brass Foil at 800° C. in Vacuo.

Type of Brass	Initial Composition	Loss in Weight, %	Decrease in Length, %
(1) <i>Slow heating</i> :			
Sb-free .	25% Zn	24.6	7.1
0.2% Sb .	27.6% Zn + 0.19% Sb	23.2	6.1
" .	"	27.5	4.6
" .	"	27.4	5.1
(2) <i>Rapid heating</i> :			
Sb-free .	25% Zn	23.4	6.5
0.2% Sb .	27.6% Zn + 0.19% Sb	24.0	6.3
" .	"	26.9	5.1
" .	"	26.2	5.4

whereas in the second set the furnace was held at temperature and the specimens were moved into the hot zone for 1 hr. The table shows that with both methods of heating most of the zinc was distilled off.

The decrease in length of the antimony-bearing material is slightly, but consistently, less than for the antimony-free material. Figs. 3 and 4 (Plate LXIX) show cross-sections of specimens of both materials, and clearly there is a greater number of holes in the antimony-bearing than in the antimony-free material, although in neither case do the holes favour the grain boundaries.

## IV.—DISCUSSION

In the case of the rods, it is clear from Figs. 1 (a) and (b) and 2 (a) and (b) that zinc diffuses mainly along the grain boundaries to the surface of the rods, where it is removed. Fig. 5 (Plate LXIX) shows that, as the zinc is removed, the cracks penetrating from the surface along the grain boundaries are preceded by the formation of holes in the boundary alone. It is only later that holes form within the grains on either side of the boundaries. These observations suggest that antimony produces its marked effect by its influence on the grain boundaries. This is in accord with the suggestion<sup>8,9</sup> that equilibrium segregation of antimony to grain boundaries takes place in copper alloys containing antimony. The influence of antimony on the grain boundaries of the foil should be the same as on the grain boundaries of the rods, yet, in the foils, where internal stresses are absent, the holes do not form preferentially at the boundaries. On the other hand, the presence of antimony increases the number of holes within the

grains. Thus, in both the rods and the foils antimony increases the formation of holes but does not alter their location. Therefore, it seems likely that antimony does not provide nuclei for hole formation, but merely increases the effect of nuclei already present, probably by reducing surface energy.

Since in the antimony-bearing foil more vacancies are precipitated in the form of holes, fewer vacancies are absorbed at grain boundaries or at dislocations than in the antimony-free foil. It would be expected, therefore, that the foil contracting least would be that containing antimony, as was observed to be the case.

It is clear from the present work that the increased loss of zinc from brass that was observed by Accary<sup>7</sup> to occur in the presence of antimony is, at least partially, due to the increased surface area resulting from the action of antimony in stimulating intergranular cracking.

### V.—CONCLUSIONS

These diffusion experiments indicate that the presence of antimony promotes the formation of holes believed to result from the precipitation of vacancies; it is therefore reasonable to explain the severe intergranular cracking in antimony-bearing alloys, previously shown to occur during deformation at elevated temperatures, as also being

due to the effect of this element on the precipitation of vacancies.

The present results demonstrate once again that, during diffusion, internal stresses are necessary for the formation at grain boundaries of holes, which eventually link together to form cracks.

### ACKNOWLEDGEMENTS

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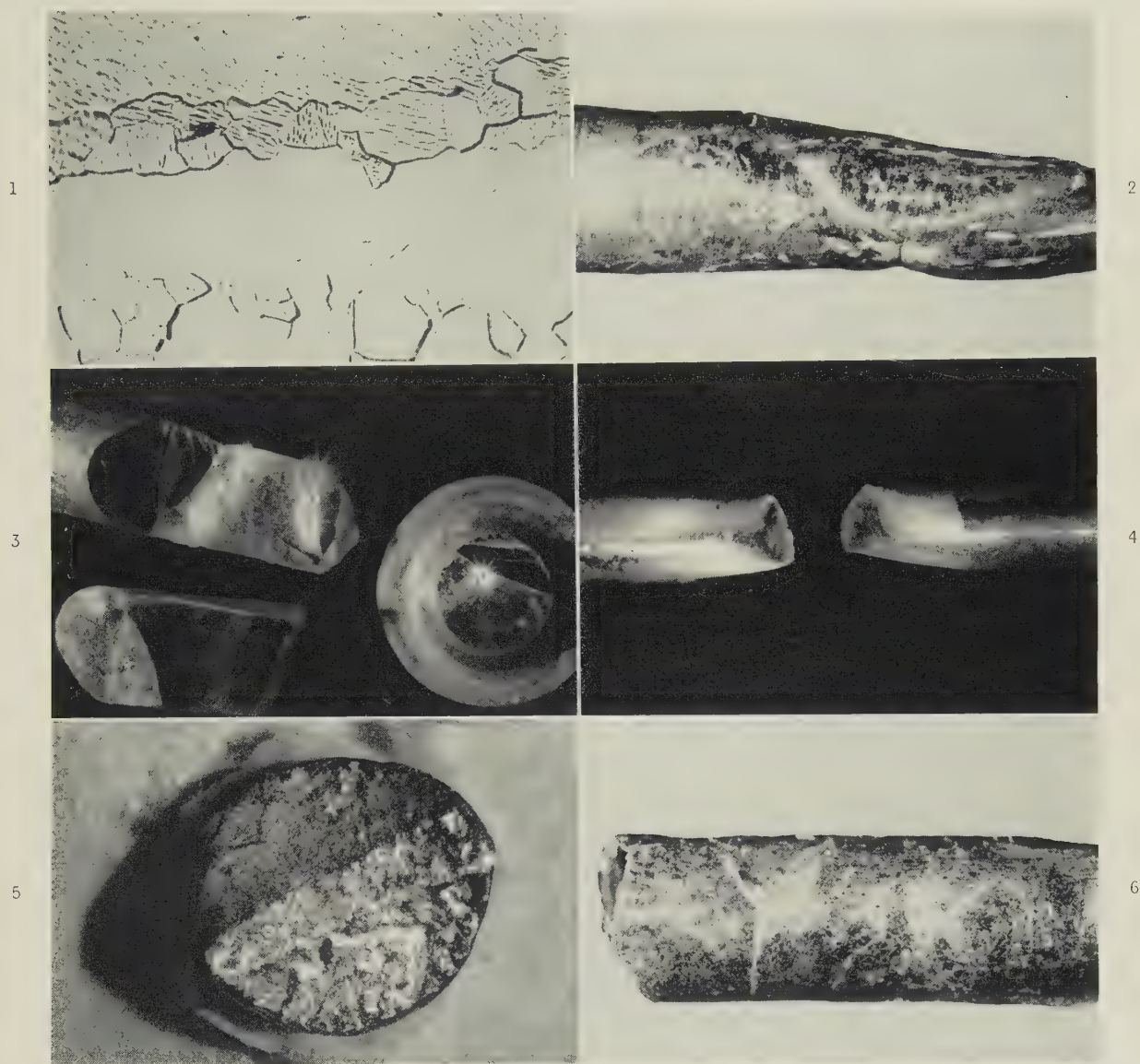
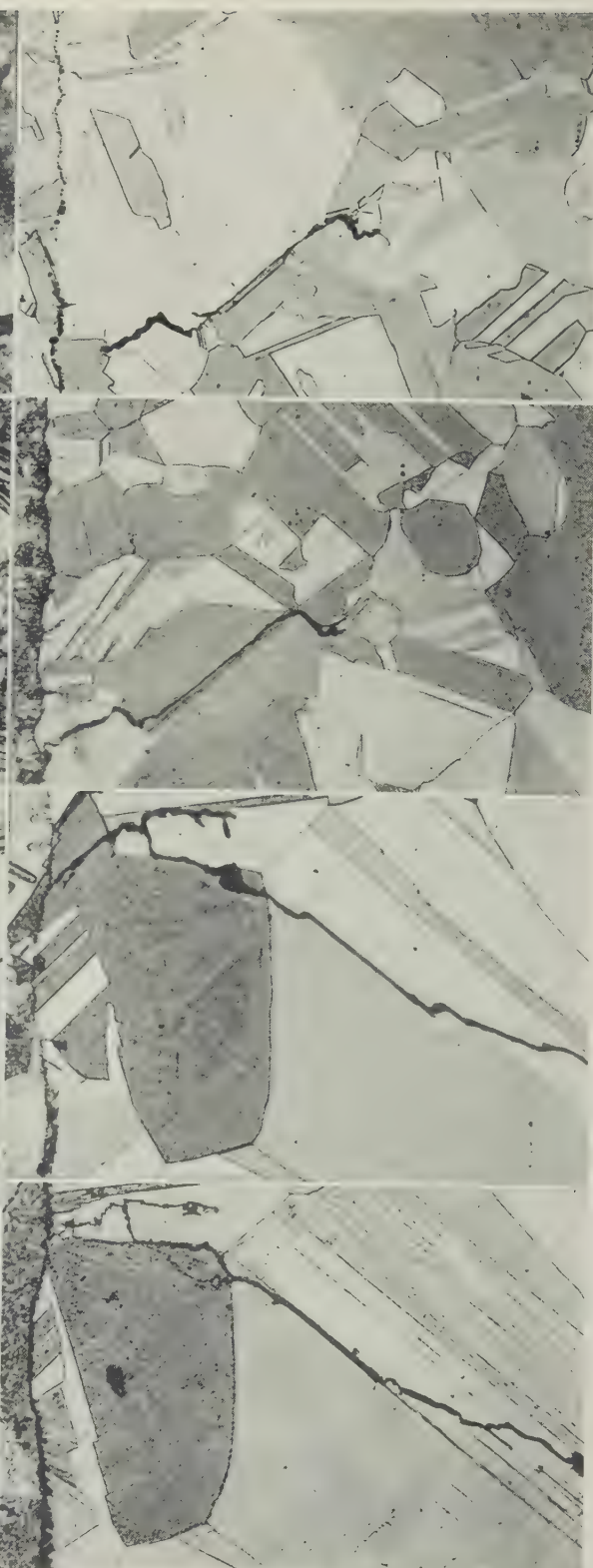
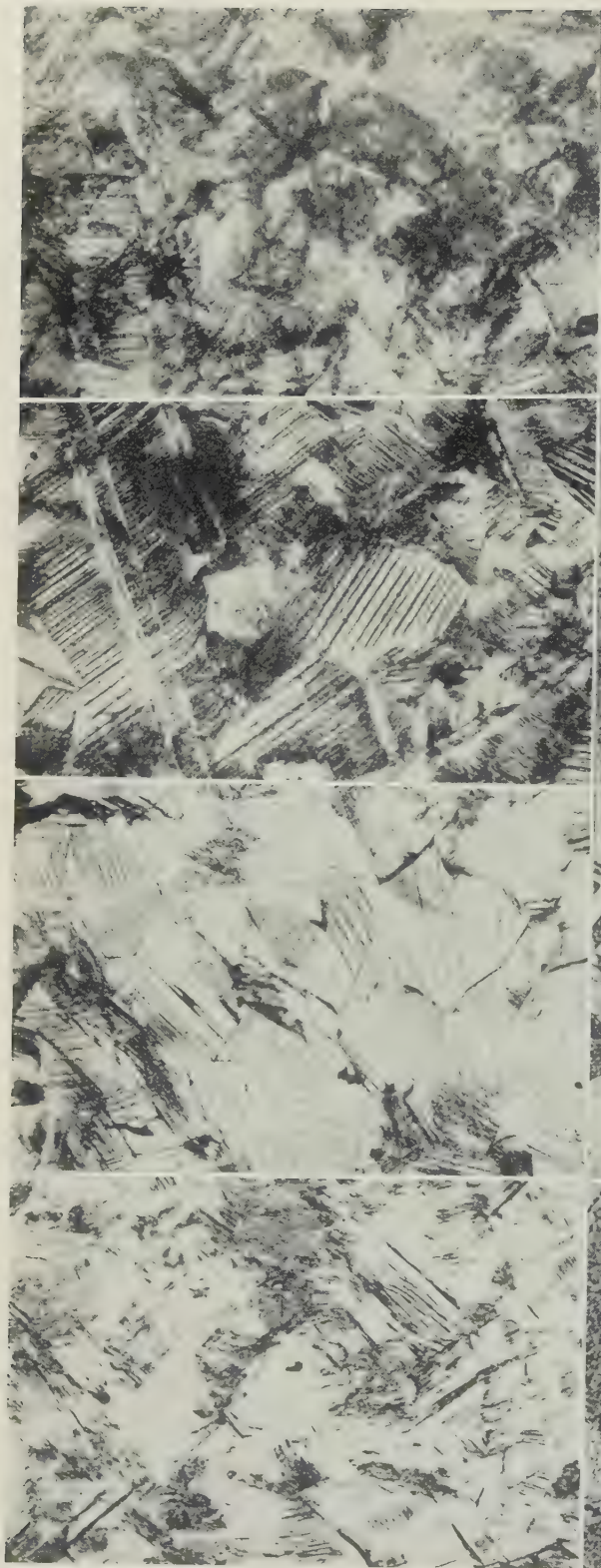
INTERGRANULAR FRACTURE OF  $\beta$ -BRASSFIG. 1.—Recrystallization Along Deformed Grain Boundaries.  $\times 360$ .

FIG. 2.—Grain-Boundary Sliding and the Beginning of a Crack in a Stress-Rupture Test. 8.

FIG. 3.—Intercrystalline Fracture on Impact of a Coarse-Grained Specimen. 4.

FIG. 4.—Impact Fracture of a Bicrystal with a Curved Boundary.  $\times 6$ .FIG. 5.—Impact Fracture of a Bicrystal with a Faceted Grain-Boundary Viewed Along the Tension Axis.  $\times 20$ .

FIG. 6.—Step Indicating Grain-Boundary Sliding near an Impact Fracture. 8.



6 7 8 9

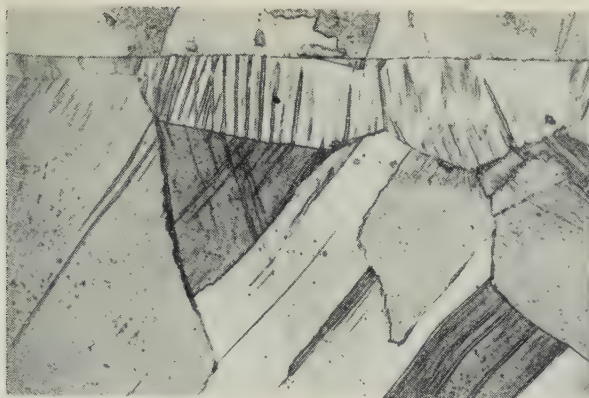
Figs. 2-5.—Surface Slip Bands Produced at Various Cyclic Stresses. As fatigued.  $\times 150$ .

FIG. 2.— $\pm 11,000$  lb./in.<sup>2</sup> (Specimen No. 3). FIG. 3.— $\pm 15,000$  lb./in.<sup>2</sup> (Specimen No. 4). FIG. 4.— $\pm 20,000$  lb./in.<sup>2</sup> (Specimen No. 4). FIG. 5.— $\pm 25,000$  lb./in.<sup>2</sup> (Specimen No. 6).

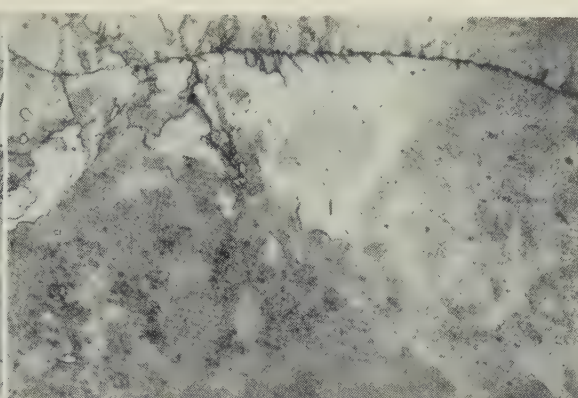
Figs. 6-9.—Effects of Annealing Low- and High-Stress Specimens at  $600^{\circ}\text{C}$ . for 1 Hr. Longitudinal sections; etched in dilute acid ferric chloride solution.  $\times 350$ .



10



11

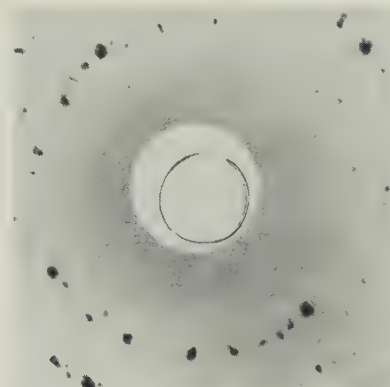


FIGS. 10 AND 11.—Surface Contours in Longitudinal Sections of a Low-Stress and a High-Stress Specimen. Etched in dilute acid ferric chloride solution.  $\times 150$ .

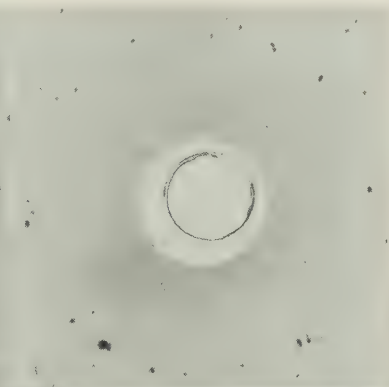
FIG. 10.—Low-stress specimen (No. 3,  $\pm 11,000$  lb./in.<sup>2</sup>).

FIG. 11.—High-stress specimen (No. 6,  $\pm 25,000$  lb./in.<sup>2</sup>).

12

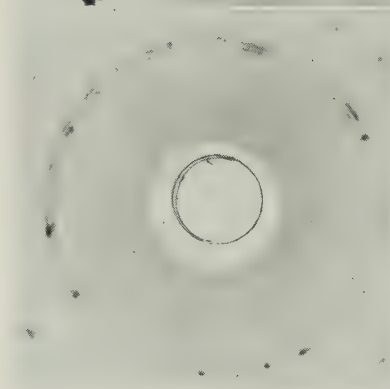


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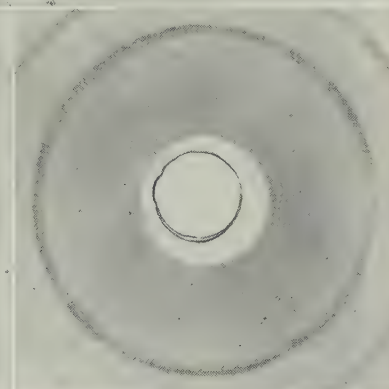


FIGS. 12-15.—X-Ray-Diffraction Patterns from Specimens Fractured at the Same Cyclic Stresses as in Figs. 2-5 (Plate LXVII), respectively.

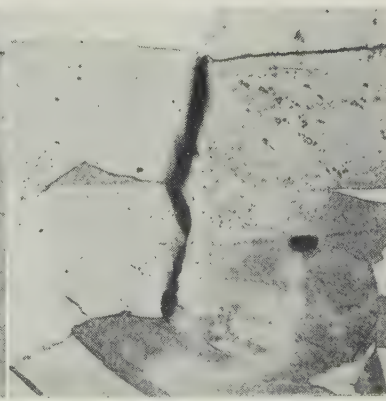
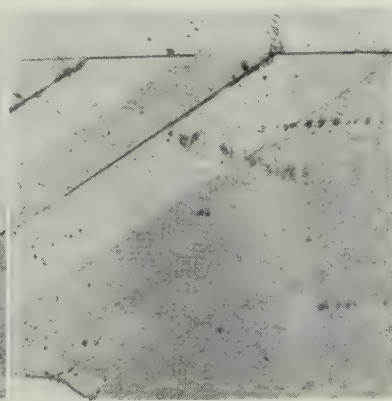
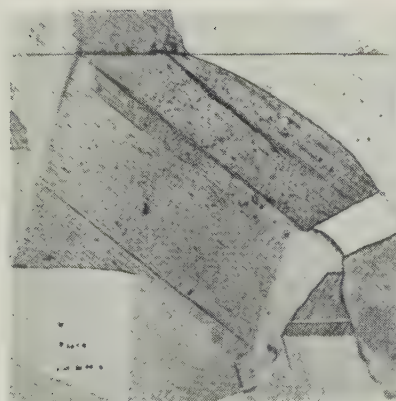
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15



FATIGUE CRACKS IN SECTIONS OF FRACTURED COPPER SPECIMENS.  $\times 500$



1

2

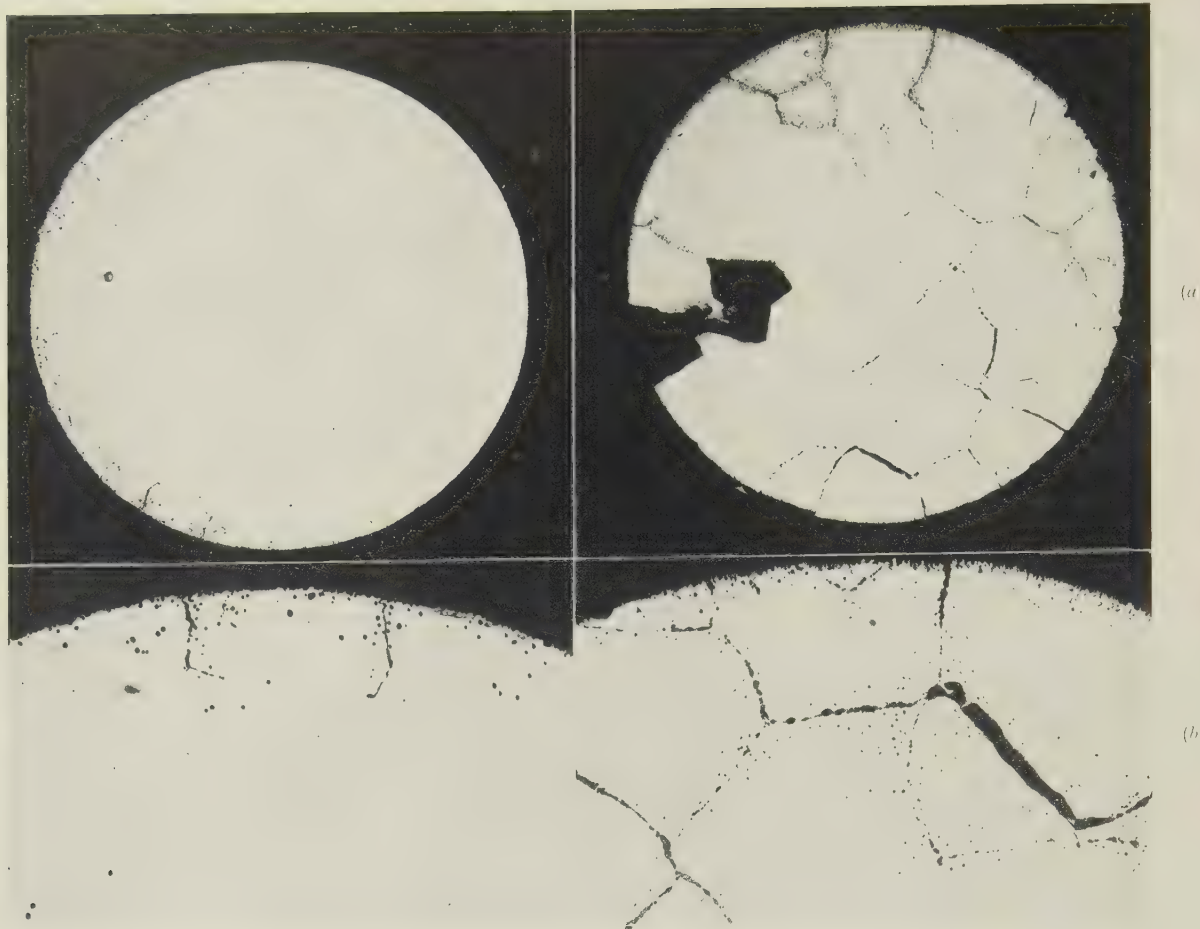
3

FIG. 1.—Low-Stress Specimen (No. 2),  $\pm 15,000$  lb./in.<sup>2</sup> Cracks following striations.

FIG. 2.—Same Specimen as in Fig. 1. Cracks following annealing-twin boundaries.

FIG. 3.—High-Stress Specimen (No. 4),  $\pm 25,000$  lb./in.<sup>2</sup>. Crack following grain boundary.

All etched in dilute acid ferric chloride solution. Protective copper plating appears at the top edge of each figure.



FIGS. 1 (a) and (b).—Antimony-Free Brass Rod Heated in *Vacuo* at 800° C. for 1 hr. Unetched sections showing few holes and slight cracking. (a)  $\times 10$ . (b)  $\times 30$ .

FIGS. 2 (a) and (b).—Antimony-Bearing Brass Rod Heated in *Vacuo* at 800° C. for 1 hr. Unetched sections showing numerous holes and extensive intergranular cracking. (a)  $\times 10$ . (b)  $\times 30$ .



FIG. 3.—Antimony-Free Foil Heated in *Vacuo* at 800° C. for 1 hr. Etched section showing holes.  $\times 750$ .

FIG. 4.—Antimony-Bearing Foil Heated in *Vacuo* at 800° C. for 1 hr. Etched section showing holes.  $\times 750$ .



FIG. 5.—Antimony-Bearing Rod Heated in *Vacuo* at 700° C. for 1 hr. Unetched section showing the progressive development, from the surface, of intergranular holes and cracks.  $\times 30$ .



# THE DAMPING BEHAVIOUR OF QUENCHED ALUMINIUM-COPPER-MAGNESIUM-SILICON ALLOYS \*

1769

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## SYNOPSIS

The transient damping maximum previously observed (*J. Inst. Metals*, 1953-54, 82, 249) during the ageing of a quenched aluminium-copper-magnesium-silicon alloy has been found to occur in supersaturated single-phase solid solutions of the same alloy series. The progressive increase of the damping effect with degree of supersaturation can be used to determine the solid-solubility limits at the temperature of solution-treatment.

Varying the quenching temperature while maintaining a constant degree of supersaturation does not affect the damping behaviour; hence it is inferred that neither vacancies nor quenching stresses play a direct part in the damping process.

## I.—INTRODUCTION

It was shown in a previous paper<sup>1</sup> that a quaternary aluminium-copper-magnesium-silicon alloy developed a transient maximum damping capacity during quench-ageing at temperatures in the range 30°–70° C. The damping was found to originate from a relaxation mechanism, characterized by the fact that its principal effect was attained at critical combinations of temperature and vibration frequency, but no convincing explanation of the cause of the loss of vibrational energy emerged.

In the present work measurements of damping capacity have been extended to alloys of the same system covering a range of compositions and quenched from a range of solution-treatment temperatures. The starting point of this investigation was the observation that none of the binary or ternary aluminium-rich combinations of aluminium, copper, magnesium, and silicon showed a damping maximum during quench-ageing. This does not, of course, prove that damping contributions with relaxation times outside the range covered by the present measurements (about four decades by temperature variation) do not exist, but, even if they do so, it is unlikely that they arise from the same cause as that detected in the work now described.

In the equilibrium state, the only structural features possibly present in the quaternary alloys which cannot exist in the ternary or binary systems are:

- (a) The quaternary compound  $Q$ .
- (b) A quaternary  $\alpha$  phase.

Measurements made to assess the relative importance of these two factors showed that the damping changes took place in the supersaturated  $\alpha$  phase and that the associated relaxation strength increased progressively with degree of supersaturation. It would therefore appear possible to determine the limits of composition of the  $\alpha$  phase at the solution-treatment temperature from damping measurements on quenched specimens. Further work is in hand to put this conclusion to a more searching test.

## II.—EXPERIMENTAL METHOD

The damping measurements were made in transverse vibration on bars measuring  $8 \times \frac{5}{8} \times 0.15$  in., at the fundamental frequency of the "free-free" mode (about 1900 c./s.), by a technique already described.<sup>1</sup> Briefly, the logarithmic decrement ( $\delta$ ) was deduced from the time taken for the amplitude of a free vibration to fall to  $\frac{1}{10}$ th of an initial value corresponding to a maximum bending stress of about 300 lb./in.<sup>2</sup>. In most of the present work damping measurements were made *in vacuo* on freshly quenched specimens which had been heated from room temperature to about 50° C. in 2 min. and thereafter maintained within  $\pm \frac{1}{2}$ ° C. of this value. At any stage during the ageing process, the damping could be measured as a function of temperature by cooling down to -60° C.

The quaternary alloys were made up from super-pure aluminium (principal impurities silicon 0.0020, iron 0.0015, copper 0.0005%); O.F.H.C. copper in the form of a super-pure aluminium-base hardener alloy containing 33½% copper; a silicon master alloy containing 11.5% silicon and 0.08% iron; and magnesium of 99.95% purity. The iron impurity in the master alloy gave rise to only 0.002% iron in the more important specimens and not more than 0.004% in any alloy. Melts of 200 g. were made in graphite crucibles, degassed with chlorine, and cast into a horizontal mild-steel mould, giving a casting  $10 \times \frac{5}{8} \times \frac{1}{2}$  in.

In each case the damping specimen was machined from the middle of the casting; at the same time three detachable feet were prepared which kept the bar out of contact with the evacuated Pyrex tube in which it was annealed. Heat-treatment was carried out in an evacuated furnace, partly to reduce the tendency for the Pyrex envelope to collapse at higher temperatures. In addition to reducing the loss of magnesium, the evacuated envelope helped to give a reproducible and effective quench, among other ways by reducing cooling in the short interval between removing the specimen from the furnace and quenching.

The soundness of the damping specimens was checked after machining by measuring three successive half-amplitude times during a single vibration decay. If

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these were not the same, i.e. if  $\delta$  varied with amplitude, the specimen was rejected.

### III.—EXPERIMENTAL RESULTS

#### 1. COMPARISON OF CAST AND EXTRUDED SPECIMENS

A preliminary test was carried out on a cast specimen of the same composition (copper 3.75, silicon 0.38, magnesium 0.63%) as the extruded quaternary alloy used in the earlier work.<sup>1</sup> The machined specimen was annealed for 2 days at 500° C., quenched, and aged at 54.6° C. The damping reached a maximum of  $\delta = 24 \times 10^{-5}$  after 2½ hr. A specimen from the extruded material similarly treated reached a maximum value of  $\delta = 26 \times 10^{-5}$  after 2½ hr. at 54° C. It was inferred from this agreement that, broadly speaking, similar results can be expected from as-cast and from extruded material.

#### 2. VARIATION OF MAGNESIUM CONTENT AT 500° C.

A set of specimens (the *A* series) was prepared, which had constant copper (4%) and silicon (0.6%) contents and magnesium contents ranging up to 3.0%. According to an extrapolation of Axon's diagram<sup>2</sup> for the system at 460° C., this includes some alloys in which the phase *Q* is present at 500° C. in the equilibrium structure and which would be supersaturated with respect to *Q* on quenching, and others, in the higher-magnesium range, which would neither show *Q* at 500° C. nor precipitate it on cooling.

The specimens were annealed separately for 2 days at 500° C., quenched in water at room temperature, and aged between 57° and 59° C. The variation in damping during this ageing process, together with the compositions and assumed structures of the specimens at 500° C., are shown in Fig. 1. As in the previous work, the damping was found to arise from a relaxation mechanism, i.e. the damping/temperature curve measured during cooling from the ageing temperature showed a peak at a temperature depending on the frequency of vibration. The peak temperatures at the frequency concerned are indicated in Fig. 2. These values are important, since they show the extent to which changes of composition affect the damping through a change in relaxation strength (height of the peak) or relaxation time (position of the peak along the temperature axis). The rise in time-dependent damping in alloys containing up to 0.9% magnesium is seen to result mainly from an increase in relaxation strength, since there is little change of peak temperature. At higher magnesium contents, both relaxation strength and time vary.

The maximum damping effect is found at about 0.9% magnesium, where *Q* predominates, but marked changes occur in both the 1.5% magnesium ( $\alpha + \text{Mg}_2\text{Si} + \theta$ ) and 3% magnesium ( $\alpha + \text{Mg}_2\text{Si} + S$ ) alloys, neither of which contains *Q* at 500° C. nor precipitates *Q* on cooling. The conclusion drawn at this stage therefore was that *Q*, which was microscopically observable in the microstructure at the solution-treatment temperature, is not responsible for the damping behaviour. (Effects at the *Q*/ $\alpha$  interface might have provided a possible explanation.) Thus, some pre-precipitation rearrangement in the  $\alpha$  phase must be the controlling factor, though it need not necessarily be one leading to the precipitation of *Q*. The fact that non-equilibrium structures of which the equilibrium diagram gives no indication may exist temporarily,

is likely to be of great importance in the interpretation of these damping changes. Indeed, a full explanation of the damping behaviour must await a more detailed picture of the stages through which the supersaturated  $\alpha$  phase passes in attaining equilibrium.

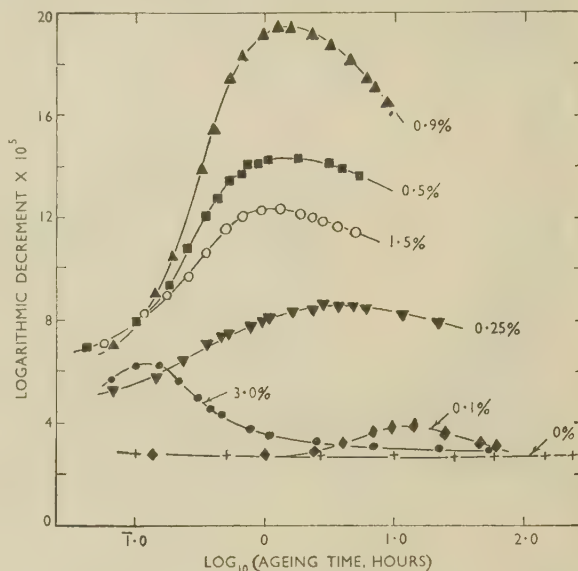


Fig. 1.—Variation of Damping During Ageing at 57°–59° C. of Alloys Solution-Treated for 2 Days at 500° C. and Quenched into Water at 15° C. All alloys contain 4% copper and 0.6% silicon; the magnesium content is given on each curve.

#### 3. VARIATION OF COMPOSITION OF THE $\alpha$ PHASE

A series of specimens (the  $\alpha$  series) was machined from castings having nominally constant copper (2.5%) and silicon (0.3%) contents and magnesium contents selected to give alloys which at the solution-treatment temperature (460°  $\pm$  2° C.) would be single-phase in the lower magnesium range and two-phase ( $\alpha + \text{Mg}_2\text{Si}$ ) at higher magnesium contents. These were annealed to equilibrium, quenched into water at room temperature, and aged at about 54° C.

Preliminary tests were made on specimen 2 $\alpha$  in order to establish the heat-treatment that would give equilibrium as reflected by the damping measurements. Fig. 3 shows the damping curves for the same specimen at 54° C. after quenching from successive treatments of 1½ hr. at 460° C., 4 days at 460° C., 4 days at 460° C. + 1 day at 500° C. + 1 day at 460° C. Stable damping had been reached after 5 days at 460° C., but to ensure absolute certainty a standardized treatment of 1 day at 460° C. + 1 day at 500° C. + 1 week at 460° C. was adopted for all subsequent tests at this temperature.

The variation of logarithmic decrement during ageing at 54° C. for the series of specimens is shown in Fig. 4. The analyses of the  $\alpha$  alloys were:

	Analysed Composition of $\alpha$ Series		
	Cu, %	Mg, %	Si, %
1 $\alpha$	2.48	0.11	0.31
2 $\alpha$	2.51	0.24	0.31
3 $\alpha$	2.48	0.35	0.30
4 $\alpha$	2.42	0.39	0.32
5 $\alpha$	2.52	0.59	0.28
6 $\alpha$	2.51	0.71	0.29
7 $\alpha$	2.47	0.33	0.15
8 $\alpha$	1.25	0.36	0.28
9 $\alpha$	2.47	0.88	0.28



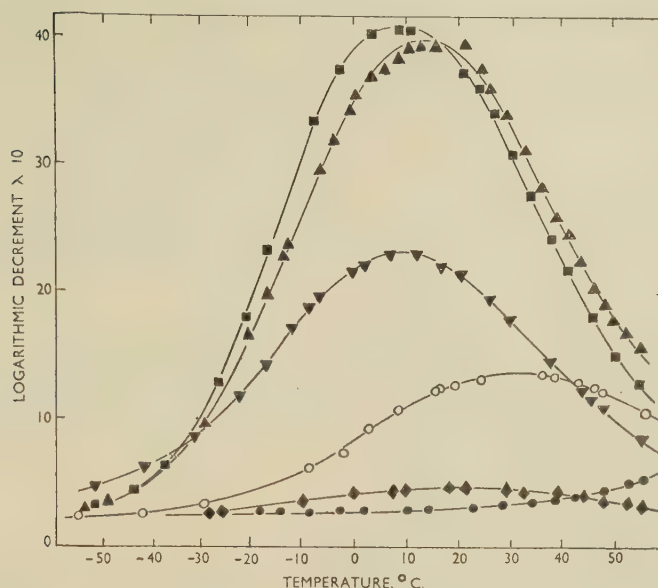


Fig. 2.—Variation of Damping with Temperature Measured During Cooling from the End Points of the Curves in Fig. 1. Vibration frequency  $\sim 1900$  c./s.

KEY TO FIGS. 1 AND 2  
Equilibrium structures at  $500^\circ\text{C}$ . are:

+	$\alpha + \text{Si} + \theta$	▼	$\alpha + \theta + Q$	○	$\alpha + \text{Mg}_2\text{Si} + \theta$
◆	$\alpha + \text{Si} + \theta + Q$	■	$\alpha + \theta + Q$	●	$\alpha + \text{Mg}_2\text{Si} + S$
		▲	$\alpha + \text{Mg}_2\text{Si} + \theta + Q$		

The analyses were carried out on drillings taken uniformly from the middle section of the bar; this procedure was based on a consideration of the distribution of vibra-

This gives rise to two contributions to the strain energy:  $U_B$ , due to bending stresses, and  $U_S$ , due to shear forces. For the specimens used in the present work,  $U_S/U_B = 0.019$ , so that  $U_S$  is not important. Between the nodes of vibration at  $x = \pm 0.5518l$ ,  $93\frac{1}{2}\%$  of the total strain energy ( $U_B + U_S$ ) is stored; therefore with linear damping,  $93\frac{1}{2}\%$  of the energy dissipation will occur in this region. Thus, only  $6\frac{1}{2}\%$  of the total dissipation takes place in the end regions, so that greater axial variations in such factors as composition and temperature can be tolerated than in the case, for example, of loaded wires in torsion, where the energy distribution is uniform.

The maximum time-dependent damping of Fig. 4 is plotted against magnesium content in Fig. 5 and shows a steep rise to a peak at 0.5% magnesium. As with the first series of alloys, the damping measured during cooling from the ageing temperature rose to a peak at a temperature which, in a given alloy, did not vary with ageing time. The peak temperatures are indicated in Fig. 4. To a first order, the ratio of temperature-dependent damping at the ageing temperature to the peak damping attained on cooling from that condition was constant. At any stage in the ageing process, therefore, the corresponding peak damping during cooling can be obtained by multiplying the measured damping by a constant factor. The second curve in Fig. 5 has been derived from the first curve in this manner and shows the same general form, with a peak at 0.55% magnesium.

The  $\alpha$  solid-solution surface at  $460^\circ\text{C}$ . derived by Axon<sup>3</sup> from extrapolation of his diagrams at 2.0, 1.2, and 0.6% silicon indicates that 0.5% magnesium must be close to the solubility limit for 2.5% copper and 0.3% silicon. The accuracy of the extrapolation is not sufficiently precise to provide an accurate check, however; an

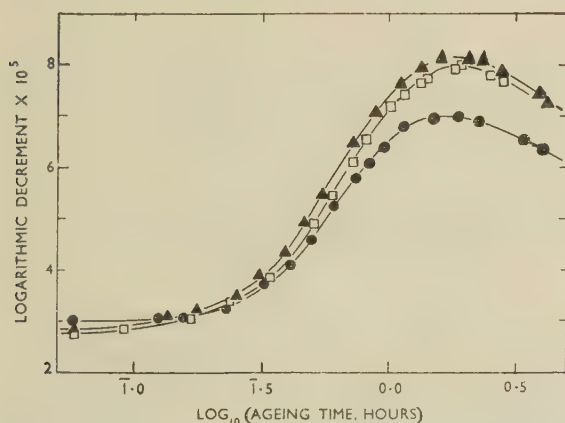


Fig. 3.—Effect of Time of Solution-Treatment on the Variation of Damping During Ageing at  $54^\circ\text{C}$ . of Specimen 2 $\alpha$  Quenched after Treatment for: ●  $1\frac{1}{2}$  hr. at  $460^\circ\text{C}$ .; ▲ a further 90 hr. at  $460^\circ\text{C}$ .; □ a further 1 day at  $500^\circ\text{C}$ . + 1 day at  $460^\circ\text{C}$ .

tional energy loss in the free-free bar. The axial variation of bending moment  $M$  with distance  $x$  from the mid-point of a bar of length  $2l$  vibrating at its fundamental frequency is:

$$M = EI\alpha m^2 (1.153 \cos mx + 0.153 \cosh mx),$$

where  $m = 2.365/l$ ,  $\alpha$  is the lateral deflection at  $x = 0$ , and  $I$  is the second moment of area of the section.

independent extrapolation of the same data by Collins<sup>4</sup> gives about 0.4% magnesium. A direct metallographic estimate was therefore made by annealing to equilibrium two small castings of composition nominally identical to

the specimens 4 $\alpha$  and 5 $\alpha$  which straddled the damping peak. 4 $\alpha$  was found to be single-phase after quenching to room temperature and 5 $\alpha$  consisted of  $\alpha$  + Mg<sub>2</sub>Si. As the analysed compositions were:

4 $\alpha$ : Si 0.32, Mg 0.46, Cu 2.50%

5 $\alpha$ : Si 0.32, Mg 0.65, Cu 2.50%,

it is clear that the solubility limit must be very close to the composition at which the maximum damping was observed, i.e. 0.55% magnesium.

#### 4. EFFECT OF SOLUTION-TREATMENT TEMPERATURE

Additional support for the conclusion that the damping behaviour shows a marked change at the solid-solubility

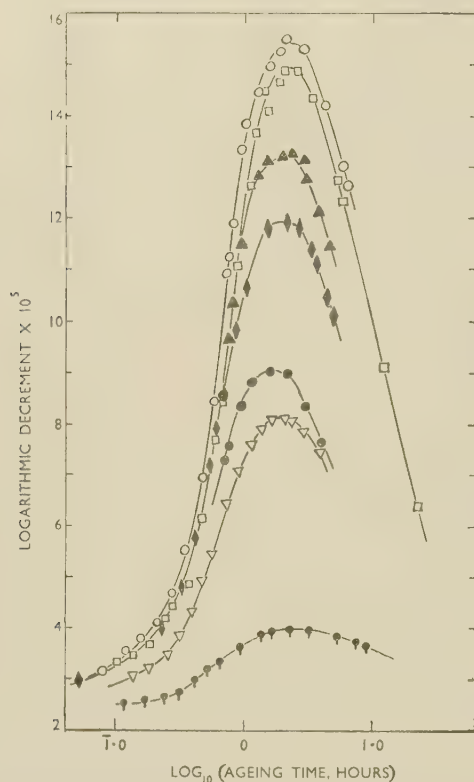


FIG. 4.—Variation of Damping During Ageing at 54° C. of the  $\alpha$  Series of Alloys Solution-Treated to Equilibrium at 460° C. and Quenched into Water at 15° C.

KEY		
Alloy	Symbol	Temp. of Max. $\delta$ During Cooling, ° C.
1 $\alpha$	●	16.5
2 $\alpha$	▽	18.5
3 $\alpha$	◆	19
4 $\alpha$	□	22
5 $\alpha$	○	22.5
6 $\alpha$	▲	27.5
9 $\alpha$	•	42

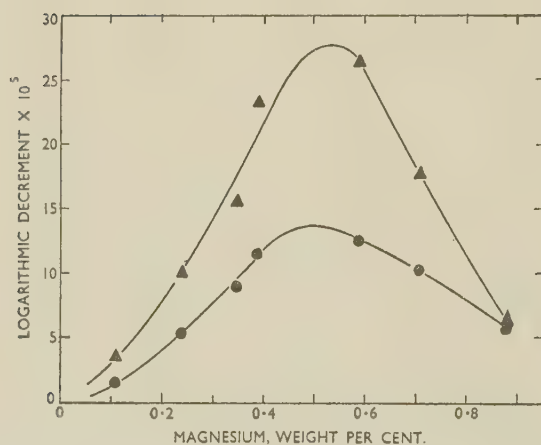


FIG. 5.—Variation with Magnesium Content of: (1) ● Measured Maximum Time-Dependent Component of Damping (Fig. 4); and (2) ▲ Deduced Maximum Temperature-Dependent Damping Attained During Cooling.

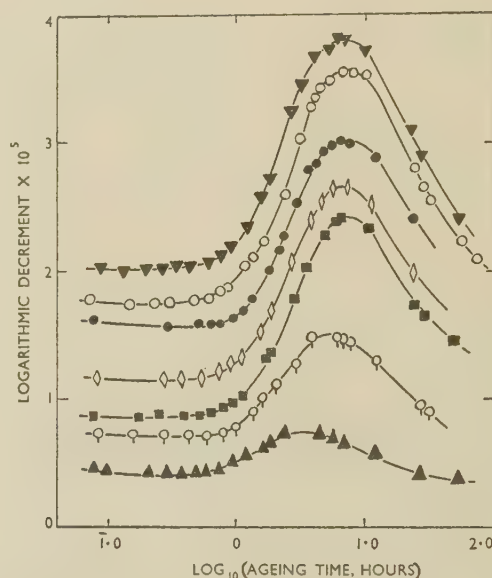


FIG. 6.—Effect of Solution-Treatment Temperature on Variation in Damping During Ageing at 54° C. of Specimen 8 $\alpha$ . The curves are displaced vertically for clarity.

KEY			
Tests were carried out in the following sequence:			
○	499° C. (2½ days)	●	597° C. (4 hr.)
▲	399° C. (5 " )	◇	Repeat 449° C. (3 days)
▼	449° C. (3 " )	◊	421° C. (9 days)
■	535° C. (36 hr.)		

limit was obtained by preparing the dilute alloy (8 $\alpha$ ) which would exist over a wide temperature range in a single-phase condition, but would be supersaturated on quenching to room temperature. A single specimen was annealed to equilibrium at successive temperatures in the range 400°–600° C., and the damping was measured during ageing at 54° C. after quenching into water at room temperature. Fig. 6 shows these results, and in Fig. 7 the maximum time-dependent damping during a test is plotted against solution-treatment temperature; the numbers above the points indicate the sequence in which the tests were carried out.

The most notable feature is the sharp drop in damping between 450° and 420° C. Above 450° C., the damping shows a progressive fall with test sequence which is ascribed to loss of magnesium during heat-treatment. This conclusion is supported by a comparison of tests 3, 5, and 6, since repeat point 6 at 450° C. is lower than



point 3 but equal to point 5 at 600° C. Failure to attain equilibrium in test 3 would have led to a higher result in test 6, because of there being a greater concentration of solute in the  $\alpha$  phase. It is therefore considered that, if the composition of the specimen were constant, the maximum damping after quenching from the range 450°–600° C. would also be constant. Metallographic examination of a specimen of composition identical to the initial composition of the damping specimen showed it to be single-phase after annealing to equilibrium at 460° C. and

effect because of its greater solubility at higher magnesium and silicon levels and has a markedly non-linear dependence on concentration.

#### IV.—DISCUSSION

It is clear from the measurements on the  $\alpha$  series of alloys that the damping peak observed in this and earlier work has its origin in the supersaturated  $\alpha$  phase. The increase of maximum damping with degree of supersaturation forms a basis for the measurement of the solid-solubility limits at the solution-treatment temperature. There are indications, however, that the damping values for the two-phase alloys are lower than would be obtained on a single-phase alloy having the same  $\alpha$  composition, i.e. the decrease in damping above 0.55% magnesium in Fig. 5 is greater than can be accounted for by the change of solute concentration. The only precipitate at 460° C. in specimens 5 $\alpha$ , 6 $\alpha$ , and 9 $\alpha$  is  $Mg_2Si$ . Hence all the copper is retained in solution, and the composition of the  $\alpha$  phase is given by the point on the  $\alpha$  boundary in the appropriate constant copper section cut by a line of gradient corresponding to  $Mg_2Si$  and passing through the composition point of the alloy. The location of the  $\alpha$  boundary is uncertain; that assumed here passes through the point (copper 2.5%, silicon 0.29%, magnesium 0.55%) determined in the present work and runs roughly parallel to the boundary in the aluminium-magnesium-silicon system.<sup>5</sup> This is about mid-way between the extrapolated estimates of Axon and of Collins.

It is clear from this analysis that an increase in magnesium content above the limit of solubility (0.55%) produces in the  $\alpha$  phase a fall in silicon content and an increase in magnesium content. If, therefore, the observed parallel fall of damping shown in Fig. 5 is to be explained purely by composition changes in the  $\alpha$  phase, the reduction of silicon content must give rise to a fall of decrement which exceeds the increase caused by the greater concentration of magnesium. More extensive damping measurements and more reliable solubility data are required to settle this point, but on the tenuous evidence available at this stage, it seems that changes of composition are insufficient to explain the fall in damping at higher magnesium concentrations.

No reliable estimate can be made of the compositions of the  $\alpha$  phase in the  $A$  series of alloys. However, the higher maximum damping attained during cooling (Fig. 2), compared with the values for the  $\alpha$  series treated at 460° C. (curve 2, Fig. 5), reflects the higher degree of supersaturation attained by quenching from 500° C.

The effect of quenching temperature on damping (Fig. 6) is important in relation to the part played by vacancies in the damping process. It is considered that at a constant degree of supersaturation the relaxation strength is independent of quenching temperature in the range 450°–600° C. If the mobility of vacancies in this temperature range allows the equilibrium vacancy concentration to be preserved even at the highest quenching rates reached in this work, i.e. if the effective quenching temperature is below 450° C., then the concentration of vacancies in the alloys quenched from 450°–600° C. would be independent of the temperature of quench. On this basis, the abrupt decrease in damping at 450° C.

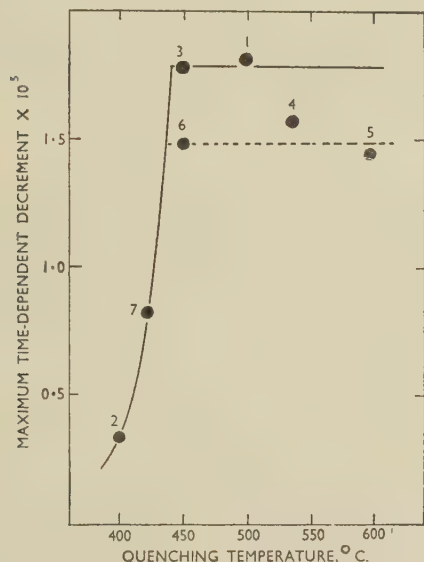


Fig. 7.—Dependence of Maximum Time-Dependent Damping in Fig. 6 on Solution-Treatment Temperature. The numbers above the points indicate the sequence of tests.

quenching, and to be multiphase ( $\alpha + Q$  with a possible trace of  $\theta$ ) after annealing for 10 days at 420° C. This observation supports the conclusion that the drop in damping between 450° and 420° C. takes place near the temperature at which the solid-solubility limit is exceeded on cooling. An approximate metallographic determination of the solidus for this alloy showed it to lie at about 620° C., i.e. well above the highest temperature used in the tests.

#### 5. EFFECT OF SILICON AND COPPER CONTENT

In order to obtain some idea of the significant composition parameter which defines the intensity of the damping change, three alloys, 3 $\alpha$ , 7 $\alpha$ , and 8 $\alpha$ , were compared. They were quenched from 460° C. and aged at 54° C., with the following results:

Alloy	Max. $\delta$ Attained During Ageing, $\times 10^{-5}$	Temp. of Peak $\delta$ During Cooling, °C.	Estimated Max. $\delta$ Attained During Cooling, $\times 10^{-5}$
3 $\alpha$	9	19	15.4
7 $\alpha$	5.85	28	9.65
8 $\alpha$	1.45	29½	1.88

Nominally, specimen 7 $\alpha$  contains half as much silicon as 3 $\alpha$ , and 8 $\alpha$  contains half as much copper as 3 $\alpha$ . From this limited evidence, it appears that on an atomic percentage basis, the influence of magnesium (Fig. 5) is greater than that of silicon. Copper has a considerable

might begin at the effective quenching temperature below which the vacancy concentration will fall and in some way bring about a reduction of damping. This hypothesis is rejected on the following grounds:

(1) The correlation between the damping discontinuity and the solid-solubility limit would be coincidental.

(2) It is difficult to believe that the vacancy concentration changes sufficiently abruptly with quenching temperature to explain the form of Fig. 7. Two examples of vacancy-sensitive effects—Maddin and Cottrell's work on the quench-hardening of pure aluminium (Table 2, p. 741 of ref. 6) and Nowick and Sladek's anelasticity measurements on silver-zinc alloys (Fig. 1, p. 136, of ref. 7)—both reflect a less abrupt change. It must be admitted, however, that Maddin and Cottrell estimate their effective quenching temperature for aluminium to be 400° C., which is close to that of the discontinuity in Fig. 7.

(3) If interchange of atoms with vacancies is involved in the damping process, a variation of relaxation time,  $\tau$ , which has not been observed, would be expected during ageing. The diffusion rate  $D$  in face-centred-cubic lattices is related to  $\tau$  approximately by  $D = a^2/12\tau$ , and according to Cottrell,  $D = Ca^2\nu e^{-U/RT}$ , where  $C$  is the vacancy concentration,  $\nu$  the atomic vibration frequency, and  $U$  is the activation energy to move a vacancy. Thus, equating  $D$ 's:

$$1/\tau = C\nu e^{-U/RT}.$$

Therefore at constant temperature  $\tau \propto 1/C$  and as  $C$  falls by vacancy decay during ageing,  $\tau$  should rise.

The relation between  $\tau$  and  $C$  is of interest in showing that the observed damping-relaxation times are too

short to be explained by atom migration over one inter-atomic distance. If  $U$  is the measured activation energy for the damping process (13,000 cal./mole), then since  $\tau = 8 \times 10^{-5}$  sec. at 300° K., a value of  $C = 0.1$  is required to satisfy the equation. This is impossibly large. Even with the value of  $U = 7500$  cal./mole used by Cottrell<sup>8</sup> to explain jerky yield in aluminium alloys,  $C = 10^{-5}$ , a value which, although feasible, is still high.

It is concluded, therefore, that the as-quenched vacancy concentration will vary with quenching temperature in the range 450°–600° C. This means that the damping behaviour is influenced neither by vacancies nor by quenching stresses, which will also vary within this temperature range. Thus, the degree of supersaturation emerges as the primary factor controlling the damping behaviour.

#### ACKNOWLEDGEMENTS

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# SOME FACILITIES FOR THE STUDY OF PLUTONIUM AND ITS ALLOYS \*

1770

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## SYNOPSIS

Five glove-boxes for the safe handling of the highly toxic and reactive metal plutonium and its alloys are described. Facilities are provided for alloy preparation, X-ray examination, heat-treatment, and metallography. The apparatus is simple, is easy to use, requires little maintenance, and can readily be modified and extended whenever necessary.

## I.—INTRODUCTION

THE hazards involved in handling plutonium have been described by Dunster and Bennelick.<sup>1</sup> In brief, the toxicity of the metal is due to its high  $\alpha$ -activity and to its ready absorption in the bones, 18% of inhaled plutonium and 70% of that entering the blood stream being retained. The  $\alpha$ -particles from this retained plutonium produce intense local damage to the bone marrow. The effective half-life of plutonium in the bone is 120 years, and hence it is a cumulative poison. The maximum permissible quantity that can safely accumulate in the body during the working lifetime (normally called one body-burden) is set at 0.6  $\mu$ g., corresponding to a particle of oxide only 46  $\mu$  in dia., i.e. a particle small enough to pass through a 300-mesh sieve. Such small quantities are difficult to detect owing to the short range of the  $\alpha$ -particles (3.68 cm. in air), and one body-burden gives only about 50 counts/sec. on the standard  $\alpha$ -probes (A.E.R.E. type 1021).

Every possible effort has thus to be made to isolate plutonium and its compounds from the laboratory; this is most conveniently done by using a glove-box, since  $\alpha$ -particles do not penetrate the box walls, the Perspex panel through which the experiment is observed, or the rubber gloves used for the necessary manipulations. These boxes are maintained at a slightly reduced pressure (—1 in. water-gauge) by the building's special extract system, thus ensuring that any leaks are into and not out of the box.

Descriptions of techniques suitable for chemical processes have been published,<sup>2,3</sup> but additional precautions are required for the safe handling of metallic plutonium. For example, Dunster and Bennelick<sup>1</sup> estimate that, under conditions where a given quantity of plutonium in solution can be safely handled, 1000 times less plutonium metal can be handled in safety. In moist air, plutonium rapidly oxidizes to a fine dust, and the principal health hazard arises from airborne contamination. The stringency of the precautions necessary can be judged from the fact that the agreed maximum permissible level (M.P.L.) of hydrogen cyanide gas in the air is 350 million times the M.P.L. for plutonium.<sup>4,5</sup>

With the quantities of plutonium normally handled

(~10 g.), no special precautions against  $\beta$ - or  $\gamma$ -radiation are taken, except that the duration of direct contact of plutonium with the gloved hand is kept below 3 hr. a week.

Facilities and techniques for handling metallic plutonium have been in course of development by the Plutonium Metallurgy Group at the Atomic Energy Research Establishment for several years. The earliest equipment was installed in large cells operated from one face. Poor accessibility led to the conception of isolated "free-standing" glove-boxes which could be operated through gloves in any one of four faces, and suites of such boxes were designed for operations such as the production of the plutonium elements for the ZEPHYR fast-reactor experiment. An access panel on each box provides for the servicing of the larger components by operators in protective "frog-suits" after the box has been sealed to an "active" workshop area. Even simple operations carried out in this way necessitate the box being out of service for several days.

Because of the amount of plutonium involved and the large number of repetitive operations to be carried out by the industrial staff the equipment in these free-standing boxes was designed to meet relatively rigid safety regulations.<sup>6,7</sup> Each box was tailor-made to contain permanently the equipment around which it was initially designed, and it afforded little flexibility for any but minor modifications. Nevertheless, the technical advantages of the boxes by comparison with the earlier large single-face cell, have led to their adoption for research facilities, particularly since manufacturing and design procedures already in being minimized the use of scientific staff. Even with this measure, however, the time taken to design, manufacture, and commission boxes was usually over a year from the conception of the experiment to the supply of the completed glove-box.

## II.—DESIGN CONSIDERATIONS

The free-standing boxes to be described supplement many of the existing facilities and were intended to be more adaptable, so that, apart from the requirements of safety, there would be little restriction on the development and testing of new experimental arrangements or methods. They represent a new departure in that the

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apparatus was developed to fit into standard glove-box shells already available.

Since the boxes were intended for research on plutonium alloys, the behaviour of which is largely unknown, only a rough outline of the type of work to be done could be foreseen. Thus, the apparatus had to be sufficiently simple and flexible to be discarded, modified, or rebuilt inside the boxes. Very little of it is therefore a permanent fixture in the box. In this sense, it is possible to regard the suite of boxes as a laboratory area for handling highly  $\alpha$ -active materials.

Experiments in glove-boxes are normally time-consuming for the following reasons. First, maintenance within a box is a lengthy procedure and holds up use of the box for its primary purpose; however, if the faulty component can be easily taken out of the box, it can be replaced and then either discarded or repaired in the active workshop—whichever is the cheaper. The removal of articles from an active box is not a simple process, however, since even an air lock will allow  $\alpha$ -active dust ("contamination") to spread into the laboratory. It is now standard practice to "post" articles in and out, using a plastic bag which can be heat-sealed (see Fig. 1). The standard A.E.R.E. components permit articles less than  $7\frac{1}{2}$  in. in outside dia. to be passed in or out of the box by the normal posting procedure. Secondly, moving from one pair of gloves to another wastes time, and it is very desirable that a completed operation, and preferably more than one, be carried out through each pair. Thirdly, specimens have to be transferred from one box to another, and though the heat-sealing into plastic bags on entering and leaving each box is not in itself a very lengthy process, it can occupy a large proportion of the total time. One solution is to connect all the boxes together by short plastic tunnels; this is obviously advantageous for production work in which the order of operation is fixed.<sup>8</sup> In all cases, however, as many consecutive operations as possible should be carried out in each box, consistent with operating from one, or at most two pairs of gloves. Finally, there is a real need to provide adequate storage space inside the box within easy reach of the operator.

An attempt has been made to apply these principles to the apparatus described, and most of the operations can now be carried out with an ease and speed comparable to similar operations in a non-active research laboratory. All features of the boxes which influence the safety of operation are nevertheless in accordance with established custom at the A.E.R.E. for handling metallic plutonium,<sup>7</sup> e.g. all liquids and gases enter the box through unions which automatically seal on disconnecting, and, to prevent activity escaping up the extract system, filters are fitted on the inside of the box so that they can be changed with safety.

The standard bag- and glove-changing procedure is illustrated in Fig. 1 (a). The usual posting-in technique is shown, for comparison, in Fig. 1 (b). The article is placed in a pouch formed by pushing in the end of the bag and the pouch is closed by heat-sealing; the bag is then extended into the box and the pouch containing the article is cut off with scissors. Articles are taken out of the box by placing them in the plastic posting bag, heat-sealing, and cutting along the seal.

The general structure of the boxes has been described by Dunster and Bennellick.<sup>1</sup> Rubber mouldings are

used to hold the Perspex faces, as in some car windows. These boxes were readily available in a standard size, but boxes with bolted-on faces would have been preferable for safety reasons had they been similarly obtainable.

To prevent oxidation of the plutonium, purified argon is continuously circulated. For some applications this is unnecessary, but, since it is essential for the more reactive alloys,<sup>6</sup> it is a great convenience to maintain permanently an inert atmosphere, particularly as the fire hazard is thereby very much reduced. With such a system of argon circulation, the leak rates of boxes must be kept reasonably small ( $<0.5\%$  of the box volume/hr. at  $-4$  in. water-gauge differential pressure). A leak of this magnitude can be found with soap and water

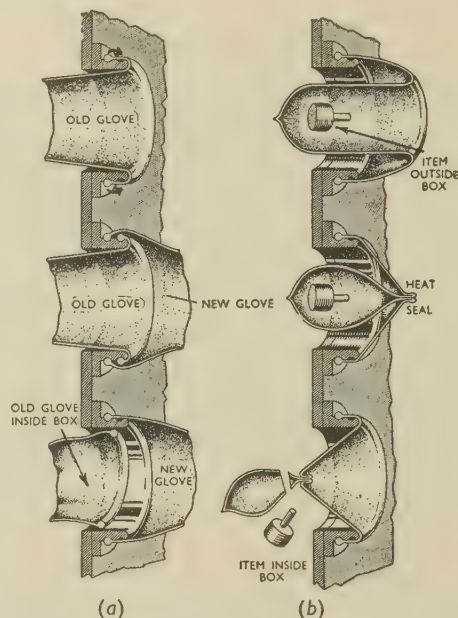


FIG. 1.—Illustrating (a) Glove-Changing Procedure; (b) Posting-In Procedure.

before "going active", if the box is placed under a slight positive pressure. This low leak rate, together with the reduced pressure inside the box, makes the spread of  $\alpha$ -contamination negligible during normal operation.

### III.—GLOVE-BOX FACILITIES

Five glove-boxes are described: for alloy preparation, X-ray examination, sealing in vacuum, heat-treatment, and metallography. The boxes for the last three operations, which form a very common sequence, have recently been connected together by short plastic tunnels. The tunnels are not permanent, but fit on to standard posting ports, so that boxes can be separated merely by heat-sealing across the tunnel and cutting along the centre of the seal.

#### 1. ALLOY-PREPARATION BOX

The box, shown in Fig. 6 (Plate LXX) contains a balance for weighing the components of the alloy to be prepared, an argon-arc furnace, and a furnace for re-



sistance-melting or annealing in vacuum or under pressure.

This box, the first to be developed, is in many ways the least satisfactory of the group. Its size (33 in.  $\times$  33 in.  $\times$  38 in. high) involves the use of more than one pair of gloves, but this disadvantage is to some extent offset by the fact that three distinct pieces of apparatus are housed in the box. For safety reasons, motors, which may be left running unattended, are housed in a compartment separated from that containing the plutonium and run in a nitrogen atmosphere. This introduces the complication of a separate box for the pumping equipment; the alternative is to run the pumps in the open laboratory and discharge the output through filters to the active extract, but the relative advantages of this procedure are not yet known.

A balance, accurate to 5 mg. and operated from the left-hand face of the box, is available for weighing alloy

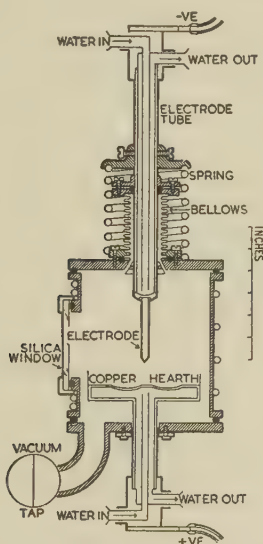


Fig. 2.—Section Through Arc Furnace.

components. The balance is of a standard design, in which weights of less than 1 g. are applied by a chain. More accurate weighings can, if necessary, be made on another balance housed in a separate box (to eliminate vibrations) connected to the back of the alloy-preparation box by a short plastic tunnel. This balance, though accurate to 0.1 mg., is ideally suited for use in a glove-box, since all weights from 0.1 to 199.9 g. are applied semi-automatically, and the value of the residual weight (0–100 mg.) is read from a projected scale.

The argon-arc furnace, shown in section in Fig. 2, is generally similar to that described by McQuillan and McQuillan,<sup>9</sup> though it differs in certain important respects. The usual projecting viewing tube has been replaced by a large flat silica window, so that the body will pass through a standard posting port; the size of the window enables the interior of the furnace to be illuminated from outside the box. The hearth units, which may be changed by unscrewing the water connection outside the furnace, are equipped with tungsten studs on which the arc can be struck. In the event of failure, the bellows unit can be discarded and replaced by undoing the O-ring seals at each end of the bellows.

The top and bottom plates are held to the body by suction against the O-rings which also provide electrical insulation. Since large quantities of potentially contaminated water cannot be discharged down the drain, water is recirculated through the hearth and electrode assemblies in series, and is cooled by a small radiator unit (car-heater type). The central tubes of the two assemblies are chosen to give a large powerful jet with very little constriction, and the cooling has proved entirely adequate at all power inputs from the 150-amp. welding generator. Standard O-ring couplings and taps are used throughout the 1-in. pumping line, and any part can be replaced if faulty. The furnace atmosphere can be isolated by a tap close to the furnace base during gettering and melting.

A hearth with three depressions for melting, and three casting troughs, is normally used, and up to six alloys are loaded at one time; the furnace is evacuated and argon is admitted to a pressure of 15 cm. mercury and gettered by melting a titanium or zirconium bead. Each alloy is melted and turned over at least four times to promote homogeneity and is finally cast into a trough, if desired.

The furnace has been used for approximate solidus determinations at high temperatures. A 1-in. molybdenum cube with a hole  $\frac{3}{4}$  in. long and  $\frac{1}{4}$  in. in dia. in one side is heated by means of the arc; the temperature of a small piece of alloy placed on a tantalum boat in this hole is determined with an optical pyrometer. This temperature is varied by adjustments to the power of the arc, and the onset of a change of shape of the specimen is taken to indicate the approximate solidus. Temperatures in the range 1000°–2000° C. can be attained and measured with a reproducibility of  $\pm 50^\circ$  C. Calibration against the melting points of pure metals indicates that the effective emissivity under these conditions is about 0.6.

A section through the resistance-melting furnace and vacuum-tight tube is shown in Fig. 3. The furnace case is small enough to pass through a standard posting port, and this means that the thermal insulation is limited. Thus water-cooling is essential to avoid overheating of the box and consequent collapse of the Perspex panels. The windings are of Nichrome on silica tubes which can be operated up to 1000° C. and readily replaced in the event of failure. Alloys can be melted or heat-treated under vacuum or in a positive pressure of argon in the stainless-steel tube. This is connected to the vacuum system by a 1-in. union and can be replaced by other metal or refractory tubes. The system has been used for making up alloys from volatile metals (under argon), for preparing alloys by the co-reduction of fluorides<sup>10</sup> and, after slight additions, for thermal analysis, dilatometry, or both.

The vacuum systems associated with the arc furnace and the resistance-heated tube are connected to a common union near the floor of the box and can be interchanged in a few minutes. The common union is on the end of the 1-in. vacuum line leading from the 1-in. diffusion pump, small 2-stage rotary pump, and vacuum gauges housed in the lower box. The diffusion pump is necessary for adequate degassing of refractories or for vacuum melting, and is a convenience for testing the arc furnace for leaks, though its inclusion would not be justified on the latter account alone. All the

components of the vacuum system can be "posted" out of the box, if necessary.

Most of the electrical connections inside the two boxes are of a permanent nature, and this has been found to complicate servicing and reduce experimental flexibility. The electrical controls are also somewhat unsatisfactory, as they are mounted in the conventional rack by the side of the box. This mounting is suitable for processes which largely involve electrical manipulation, but for most research purposes the system used for the remainder of the boxes is preferable.

The upper port, illustrated in Fig. 6 (Plate LXX), is for a simplified posting-in procedure, employing short 6-in.-dia. plastic bags. The article to be transferred into the box is placed in a new bag which is clipped on over the old one. The latter can then be taken into the

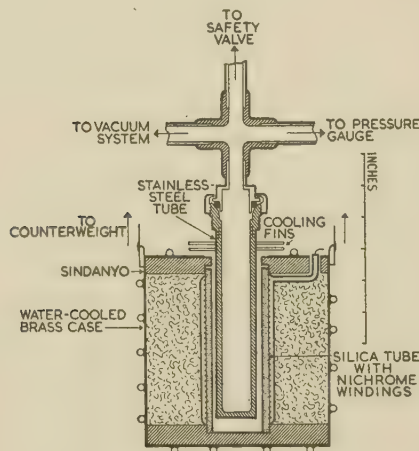


Fig. 3.—Section Through the Resistance Melting Furnace and Co-reduction Apparatus.

box together with the article. Similar posting-in can be done during the identical operation involved in changing a glove (see Fig. 1).

## 2. X-RAY-SPECIMEN PREPARATION AND VACUUM-SEALING BOX

This box,  $39 \times 24 \times 29$  in. high, contains equipment for the preparation, sealing in vacuum, and stress-relieving of filings, and for preparing the X-ray specimens. Other small alloy specimens can be sealed in vacuum for heat-treatment. Cutting up or cleaning of billets of plutonium or of alloy beads is also normally carried out in this box.

The filings are prepared under trichlorethylene (as an extra precaution against oxidation). Iron contamination is removed with a magnet, and the dried filings are transferred to a tube, as shown in Fig. 4, where they fall past the constriction. A number of glass beads for identification, uranium turnings as a getter, and a glass rod are added before the tube is connected to a rotary vacuum pump by an O-ring adaptor. It was considered justifiable to have the pump in the same box, as it is used only for short periods when an operator is present, so that in an emergency appropriate action can be taken immediately. Gettering the vacuum with heated uranium

is preferred to using a diffusion pump, since it is simpler and gives satisfactory results.

The hazard involved in either a fire or an explosion precludes the use of a gas torch for sealing off. Instead, a small resistance furnace is used (see Fig. 4), controlled

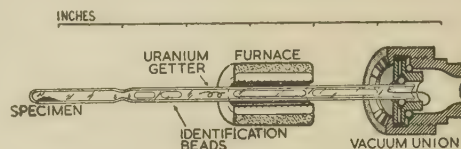


Fig. 4.—Section Through the Sealing-Off Equipment.

by a Variac outside the box. This has proved satisfactory for both Pyrex (for annealing to  $600^\circ\text{C}.$ ) and aluminium silicate glass (up to  $800^\circ\text{C}.$ ). The loaded tube is pumped to less than  $50\ \mu$  pressure, and the first seal is made on to the glass rod. The getter is then heated before the last seal is made at the constriction.

A water-cooled furnace, similar to that in the alloy-preparation box, is used for stress-relieving the filings, usually at  $500^\circ\text{C}.$  X-ray specimens, in the form of a flat disc for the Guinier camera, are prepared by sprinkling the filings on to celluloid mounted on a brass annulus. The filings are held in place and protected from oxidation by Canada balsam. No trace of oxidation or of contamination from the glass has yet been detected in over 100 specimens examined shortly after preparation. After some months' storage in the air-filled camera box, however, oxide was found on some specimens.

The electrical connections to apparatus inside the box are made by standard 3-pin, 5-amp. plugs. Four 3-pin sockets are provided inside the box, and these may be connected by wandering 3-pin plugs to the electrical control panel. This is placed beneath the box, where switches and even Variac knobs can be operated by the knees. All apparatus, when not in use, is unplugged inside the box to prevent its being inadvertently switched on. A six-way terminal block inside the box, connected with a similar one outside, provides for thermocouple wiring. This simple system has been of value in giving great flexibility in use and has been copied on the other boxes.

## 3. X-RAY-CAMERA BOX

A focusing transmission camera was chosen, primarily because it gives accurate  $d$  values at low Bragg angles and hence is very suitable for structure determinations. It has also the important secondary advantage that it is particularly simple to use with a glove-box.

The geometry of the camera, shown in Fig. 5, is based on a design by Hägg described in detail by D'Eye.<sup>11</sup> The monochromatic X-rays reflected from a curved quartz crystal converge to a point on the cylindrical film, where the  $K\alpha_1$  and  $K\alpha_2$  components are resolved.

The specimen lies on the same circle as the film to give focusing of the reflected rays, and should ideally conform to this circle; however, since only a small area ( $2 \times 2$  mm.) is irradiated, a flat specimen, which introduces negligible defocusing, is used. The specimen disc clips on to its holder, which fits on to the base-plate (shown in Fig. 5). This is enclosed in an extension



to the glove-box; X-ray tube, monochromator, and film holder are outside the box and do not become contaminated.

The use of monochromatic radiation results in a very low background intensity, and so enables very weak lines to be detected. It also gives a very low instrumental broadening, so that close doublets are resolved, and provides nearly achromatic conditions at low angles where accuracy of measurement is essential. Molybdenum  $K\alpha$  radiation was chosen because of its high penetration and because fluorescent radiation, excited in most specimens, is filtered out by the celluloid mount.

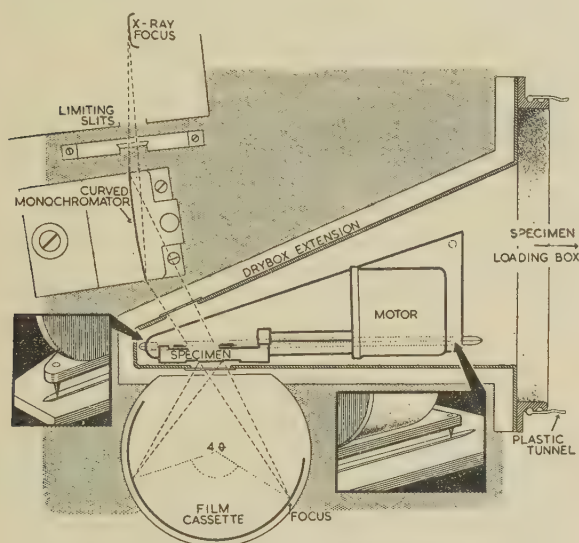


FIG. 5.—The Arrangement of the Guinier Focusing Camera.

In plutonium  $\mu/\rho$  is approximately  $53 \pm 3 \text{ cm}^2 \text{ g}^{-1}$  for  $\text{MoK}\alpha$  and 377 for  $\text{CuK}\alpha$ . This high penetration seemed desirable at the time to reduce the effect of oxide. However, with the specimen-preparation system described previously, this is perhaps unnecessary, since no oxidation has been observed.

The only disadvantage of  $\text{MoK}\alpha$  radiation relative to  $\text{CuK}\alpha$  is that it halves the dispersion of the lines, but this is largely compensated for by the use of a focusing camera. Lines are recorded on one side only of the straight-through beam, and film-shrinkage errors are eliminated by printing a scale on the film before development. The lines on the films from this camera are so sharp that a magnification of twelve can generally be used in measuring them. Thus, the effective diameter of the camera is considerably greater than its actual value of 8.0 cm.

The camera has two disadvantages; first, accurate lattice parameters cannot be determined by extrapolation to  $\theta = 90^\circ$ ; secondly, initial setting up is more laborious than it is for conventional cameras. It has not yet proved necessary in our research to determine lattice parameters to an accuracy higher than 0.005 Å. It is much more important that all the  $d$ -values should be as accurate as this. In the event of higher precision being required, a back-reflection camera to accommodate the same specimens could easily be attached to the box. The time involved in first setting up the camera is greater than that taken with the usual powder cameras, but the subsequent ease of use makes this worth while; in

particular, no adjustment of specimen or film position is necessary, and specimens are very robust, requiring no exceptional care in handling.

#### 4. METALLOGRAPHY BOX

This box,  $39 \times 24 \times 29$  in. high, shown in Fig. 7 (Plate LXX), contains equipment for grinding, mechanical or electrolytic polishing, etching, and microscopic examination.

Specimens, mounted where necessary in a cold-setting resin, are ground on silicon carbide papers moistened with paraffin. With high-quality papers, this operation can be carried out rapidly by hand and is normally complete in less than 5 min. In order to avoid abrasion of the gloves during grinding or polishing, the specimens are held in a small jig. This allows the specimen to pivot in two directions about a point close to its surface, so that the specimen does not rock.

To provide a simple variable-speed drive for a polishing wheel without the use of gears or belt drives, a brush motor controlled by an external Variac was chosen. A  $\frac{1}{4}$ -in. portable electric drill is a cheap and readily replaceable unit for this purpose and has excellent torque characteristics at low speeds. The drill was converted by mounting it upside down on its stand and providing a splash guard. The pads are 3 in. in dia. and have a  $\frac{1}{4}$ -in.-dia. shaft which fits in the drill chuck. Metal polish and diamond paste ( $1 \mu$ ) have been used.

Electropolishing is carried out in a small cell having a nickel cathode; with small specimens, a contact is cast into the resin. Many electrolytes have been tried, but a 10% solution of perchloric acid in butyl cellusolve and various mixtures of phosphoric and sulphuric acids have proved particularly successful. The current is provided by a Variac and a full-wave rectifier. The Variac can be operated by the knees, the voltage and current being indicated by meters inside the box. Etching is carried out by immersion in the etching medium or by applying the latter with a camel-hair brush.

It is a very great advantage to be able to examine the specimen readily at any stage during the final polishing or etching; hence it is desirable to have a microscope for use with this box. Because of corrosive fumes and servicing difficulties, it is not practicable to place a high-quality microscope inside the box with the eyepiece tube sealed through the box wall. The removal of polished specimens and their decontamination before examination in the open laboratory or a fume hood would be hazardous and offers no significant saving in time over the use of a separate box for housing the microscope. This difficulty was solved by viewing the specimen through a thin window, all the optical components being outside the box. The window material finally chosen was clear plastic P.V.C. sheet, 0.010 in. thick. Though this is perhaps not an ideal optical material, it is satisfactory in use and has the added advantages that it is tough and unbreakable; by using a bag of the plastic which fits on a standard glove port, it is readily changed when it becomes dirty.

To obtain good "optical contact" between the polished face and the plastic, the specimen is moistened with a drop of immersion oil before being placed in the bag. Focusing, lens changes, and movement of the

microscope stage are then possible in the usual way. There is no noticeable loss of contrast, and all lenses, up to and including oil-immersion lenses, give satisfactory definition. Though a metallurgical bench microscope was used for some months with this box, an inverted microscope has proved to be much more convenient because levelling of the specimen is automatic. Some photomicrographs which illustrate the quality and clarity of the results obtainable at various magnifications are reproduced in Fig. 8 (Plate LXX).

#### 5. THE ANNEALING BOX

This box,  $39 \times 24 \times 29$  in. high, contains four furnaces with water-cooled shells of design similar to that described earlier, except that a longer furnace tube has been employed to give a more uniform temperature distribution. Each furnace is controlled by a small Variac fed from a constant-voltage source, and the temperature, indicated on millivoltmeters mounted on top of the box and visible to the operator, is constant to  $\pm 2^\circ$  at  $700^\circ\text{C}$ . The effects of any temperature gradients are reduced by placing the specimen capsules and thermocouples in 4-in. copper blocks in the central region of each furnace. The temperature of any copper block can be checked with a platinum/platinum-13% rhodium thermocouple.

With one recirculator providing the cooling and with all four furnaces running at  $850^\circ\text{C}$ ., the temperature rise inside the box is less than  $5^\circ\text{C}$ . and the temperature rise of the cooling water is less than  $15^\circ\text{C}$ . There is thus no danger of accidental overheating and subsequent softening of the Perspex panels, unless the recirculator fails; a water-flow-operated relay is provided to switch off all furnaces in such an event. As an additional safeguard, there is also a thermostat in the top of the box which switches off the furnaces if the box temperature rises above  $35^\circ\text{C}$ .

Sufficient floor space is available between the furnaces and the front of the box for manipulations such as loading the furnaces and quenching the specimens. Though no other operations are at present planned for this box, asbestos shelves have been provided on the back face to house additional equipment and tools.

#### IV.—CONCLUSIONS

The suite of boxes described has proved easier to use than was expected and has demonstrated that, at least for the small-scale operations discussed here, glove-box experiments can be carried out at reasonable speed, though making the apparatus safe and reliable before the experiment and the provision of the glove-

boxes themselves, takes much more time than is necessary in non-active laboratories. In view of the effort needed in organizing experimental facilities, it is particularly important that equipment should be capable of general, in addition to special, use. This is possible with most of the equipment described. For example, the system of metallography was tried originally in the X-ray-specimen-preparation and vacuum-sealing box, the inspection bag being fitted to the quick-posting port. When the various demands on this box interfered with the flow of work, all the metallographic equipment, by then highly contaminated, was transferred to its present box by the usual posting system. The "polishing machine" is still used as a drill whenever necessary, and it has also been used with a grindstone for touching up arc-furnace electrode tips.

It must be emphasized that the requirements of safety override all other considerations, in both the design and use of the equipment in these glove-boxes, and, with the simple apparatus described, this has not introduced insurmountable difficulties. As with other glove-box work, all users must have a strong sense of responsibility and a clear understanding of the hazards involved, both in their own interests and those of their fellow workers.

#### ACKNOWLEDGEMENTS

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# THE FORMATION OF KINK BANDS DURING THE COMPRESSION OF POLYCRYSTALLINE 70:30 BRASS\*

1771

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## SYNOPSIS

Deformation bands, found in polycrystalline 70:30 brass after comparatively small strains had been introduced by rapid compression, have been investigated by the metallographic examination of sections of the deformed specimens. In all cases, at least one of the slip systems passing through the bands is bent at the edges, and it is concluded that they are of a kink-band type. It is possible that these kink bands are a major inhomogeneity resulting from grain interaction during the deformation of polycrystals. Features similar to bands of secondary slip are observed when the compression is sufficient for slip-band indications to develop, but copious slip-line indications can always be developed in the apparently deformation-free areas, and it is concluded that these features are similar to the kink bands described above. It is thought that bands of secondary slip of the type reported as being deficient in primary slip are unlikely to occur in polycrystalline specimens. The kink bands are found to be associated with deformation conditions which favour development within the individual grains of single systems of indications of lamellar slip bands, although indications of multiple systems of single slip lines are always present.

## I.—INTRODUCTION

DURING an investigation of the effect of deformation temperature on the development of strain markings in compressed polycrystalline  $\alpha$ -brass,<sup>1</sup> inhomogeneities other than the slip-line and slip-band indications previously described<sup>2,3</sup> have been observed. In particular, it has been found that differentially coloured bands are present in many of the grains of lightly deformed specimens after metallographic etching and that when the deformation has been high enough to result in the development of slip-band indications, they, too, appear in banded regions within the grains. The purpose of the work described in the present paper was to investigate the nature of these inhomogeneities and to determine some of the conditions associated with their development.

## II.—EXPERIMENTAL METHODS

Cylinders (0.5 in. in dia.  $\times$  0.375 in. long) cut from polycrystalline brass rod containing 29.9% zinc were annealed for 36 hr. at 850° C. to produce a coarse grain-size (approx. 2.5 mm. mean grain dia.). The cylinders were compressed by amounts varying from 1 to 40% by a single hammer blow. The majority of the specimens were deformed at room temperature (nominally 20° C.), but additional specimens were also compressed at 300° C. and at -183° C. in order to obtain some indication of the effects of the temperature of deformation. In the former case the cylinders were compressed in a container maintained at the deformation temperature, and in the latter case they were compressed immediately after removal from liquid oxygen.

The compressed buttons were sectioned diametrically and polished mechanically by methods<sup>4</sup> known not to introduce any detectable strain in the surface.<sup>5</sup> Finish polishing was carried out by electrolytic means.<sup>6</sup> Two etching methods were employed, namely, the ferric chloride reagent when the specimen was to be examined for the presence of the differentially coloured areas or of slip-band indications, and the high-sensitivity electrolytic thiosulphate method<sup>6</sup> when it was to be examined for the presence of slip-line indications. Details of these etching methods have been given elsewhere.<sup>2</sup>

## III.—NATURE OF THE INHOMOGENEITIES

### 1. IDENTIFICATION

When the deformation was not sufficient to produce slip-band indications, the inhomogeneities observed after etching in the ferric chloride reagent took the form of differentially coloured regions which appeared mostly in the lighter-etching grains (Fig. 1, Plate LXXI). These regions were diffuse and of irregular form after small deformations, but, as the deformation increased, they became progressively more band-like in appearance, and the differentiation between the band and the parent grain became sharper. In well-developed cases, a number of parallel coloured bands were observed in a single grain (Fig. 2, Plate LXXI). Where such bands were normal, or approximately normal, to narrow twins, the twins were often bent sharply at each edge of the band (Fig. 2, Plate LXXI, and Fig. 11, Plate LXXII); the etching contrast between the band and the matrix was then reversed in the twinned area. Usually, there

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was only one set of primary bands within a particular grain although secondary bands were often present within the primary bands. Many instances were observed where the bands appeared to have been initiated at a point where the crystallographic nature of the grain boundary altered (Fig. 14, Plate LXXII), and the bands in one grain sometimes appeared to have induced the formation of bands in an adjoining grain (Fig. 14).

The differential colour etching of the bands suggested that the orientation of these areas differed locally from that of the parent grain. This conclusion was confirmed by examination of the etched surface under polarized light and sensitive-tint-plate illumination, when the bands appeared in strong contrast with respect to the parent grain (cf. Figs. 10 and 12, Plate LXXII). This was the most sensitive method of detecting the bands, and indicates that the crystallographic etch facets developed in the bands during etching are oriented differently from those in the parent grain.<sup>7</sup> In both their form and response to polarized light, they are similar to those observed by Woodard<sup>8</sup> in elongated polycrystalline 'Monel' metal, while in form and etching characteristics they are similar to those observed by Barrett<sup>9</sup> in compressed polycrystalline  $\beta$ -brass. Bands of similar form have also been observed in elongated polycrystalline magnesium,<sup>10</sup> and in compressed polycrystalline copper<sup>1</sup> and zinc.<sup>11</sup> It is generally agreed that the features are deformation bands of some type.

In most previous investigations, the only method available of determining the relationship between these bands and the accompanying slip has been to develop fresh slip-line markings on a metallographic section. In the present instance, however, it was possible to develop indications at the sites of virtually all the pre-existing slip planes by etching by the electrolytic thiosulphate method. It was then found that at least one system of slip-line indications was kinked or bent at the edges of the band; this was usually a system which was approximately normal to the band edge. For example, a portion of the field of Fig. 2 (Plate LXXI) is shown in Fig. 4 (Plate LXXI) after repolishing and etching to develop slip-line indications; the set of indications parallel to the twin is sharply bent at positions corresponding to the edges of the coloured bands shown in Fig. 2. The bending was even more clearly discernible in fields such as that of Fig. 3 (Plate LXXI), where only one system of indications was prominent. In most cases, the bend at the edge of the band was gentle, as shown in Fig. 4 (Plate LXXI). Multiple systems of slip-line indications were present in all areas of the grains, but the predominant system of indications varied from band to band.

It is concluded from these observations that these differentially coloured areas are kink bands, at least in the sense that they are bounded by regions in which the slip planes have kinked or bent; whether or not they can be regarded as kink bands of the classical type<sup>12-14</sup> will be discussed later. For the present, however, they will be referred to as such.

When the deformation was sufficient for the development of slip-band indications, the individual grains were often divided into band-like regions by zones of slip-band indications (Fig. 5, Plate LXXI), or into broad bands of indications separated either by regions free from indications (Figs. 6 and 7, Plate LXXI), or by areas in which the indications developed on another system.

When these specimens were repolished and etched by the electrolytic thiosulphate method, it was again found that multiple systems of slip-line indications were developed in all portions of the grains. The predominant system of slip-line indications in the areas free from slip-band indications differed from that of the slip-band indications in the adjoining bands, but the essential kinking of the slip-line indications at the edges of the bands was always observed. For example, the vertical groups of broad slip-band indications in the field of Fig. 8 (Plate LXXI) would have been etched as such by the ferric chloride reagent; the adjoining areas, which now contain slip-line indications on another system, would have been unattacked, as in Fig. 6 (Plate LXXI). Note that the group of slip-band indications has developed in a kink band of the same type as those illustrated in Figs. 2 and 3 (Plate LXXI).

The ends of the slip-band indications were also curved in many cases (Fig. 5, Plate LXXI), and secondary systems of kinking were observed in some areas containing slip-band indications (Fig. 7, Plate LXXI). Frequently, these bands were associated with differentially coloured bands of the type discussed above (Fig. 5, Plate LXXI). In these cases, occasional slip-band indications extended completely across the coloured regions, but even where they occurred only at the opposite edges, it was apparent that they had usually developed on the same group of slip planes (Fig. 5, Plate LXXI). It is concluded that, despite the considerable differences in appearance, the two features are aspects of the same phenomenon, the only difference being that in the second type lamellar slip bands have formed at certain positions.

## 2. FACTORS INFLUENCING DEVELOPMENT

The characteristics of the kink bands depended on both the strain and the temperature of deformation. At room temperature, the bands were first observed at about 2% compression; they were then of indefinite shape, could be detected only under polarized light (Fig. 9, Plate LXXII), and were present in less than 10% of the grains. By about 8% compression, however, they were present in all grains, had assumed a definite banded appearance, and could be detected in bright-field illumination. The number of bands developed in individual grains increased with increasing strain (Fig. 10, Plate LXXII) until, by about 20% compression, the bands were so numerous and interpenetrated that the structure became very confused (Fig. 11, Plate LXXII).

The effect of increasing the deformation temperature appeared to be as follows: (a) the incidence of the bands was not significantly affected, (b) the bands became narrower and more sharply defined (Figs. 10, 13, and 14, Plate LXXII), (c) the kinking at the edges of the bands was greater and less abrupt, i.e., the bending took place over a wider area, (d) the bands became more curved (cf. Figs. 13 and 14, Plate LXXII), (e) slip-band indications, when present, tended to occur preferentially at the edges of the kink bands (cf. Figs. 5 and 7, Plate LXXI).

Kink bands of the type discussed above were not noted by Samuels<sup>2</sup> in his original investigation. His specimens have been re-examined in the light of the above results, and it has been found that only a few poorly defined bands were present, polarized light being required for



their detection. A further major difference between the two sets of specimens was that, whereas only single systems of slip-band indications were developed in the individual grains of the present series, grains containing multiple systems of indications were common in Samuels' specimens. Definite kink bands were never observed in grains containing multiple systems of slip-band indications, and it seems that the development of multiple systems of slip bands precludes kinking. On the other hand, multiple systems of slip lines are found under all circumstances, and obviously they do not influence kinking.

#### IV.—DISCUSSION

Work carried out on single-crystal specimens suggests that the deformation bands observed in the present experiments could belong to one or both of two types, namely, "kink bands"<sup>12-14</sup> or "bands of secondary slip"<sup>13,15</sup>. The outstanding characteristics of the present bands is that, in all cases, at least one system of slip lines had kinked or bent prominently at the edges of the band. Although features were observed which superficially resembled bands of secondary slip, more detailed observation established that these were associated also with prominent kinking on at least one slip plane. The work of Kuhlman-Wilsdorf and Wilsdorf<sup>16</sup> and of Samuels and Hatherly<sup>3</sup> has also indicated that the probability of finding areas in polycrystalline specimens which are really devoid of systems of single slip planes is extremely remote, even after very small deformation. Areas in which slip-line indications could not be developed were never observed in the present experiments. All the features noted here must therefore be regarded as being of a kink-band type.

In view of this, the similar metallographic features previously observed in deformed polycrystalline specimens of aluminium,<sup>13</sup> 'Monel' metal,<sup>8</sup>  $\beta$ -brass,<sup>9</sup> magnesium,<sup>10</sup> and zinc<sup>11</sup> are also likely to be kink bands. It is also probable that the features described previously by Boas and Ogilvie<sup>17</sup> in deformed polycrystalline brass are the same as the kink bands discussed here. If this is so, kink bands must be regarded as a major inhomogeneity of deformation resulting from grain interaction. Calnan<sup>15</sup> has, in fact, suggested on theoretical grounds that the formation of kink bands could account completely for the maintenance of cohesion at the grain boundaries of polycrystals during deformation. The importance of grain interaction in the formation of kink bands is emphasized by the fact that simple kink bands have not been detected in single-crystal specimens of 70 : 30 brass; features akin to kink bands have been observed by Murphy and Calnan,<sup>18</sup> but these were developed only after large deformation, and they did not fulfil the normal crystallographic requirements. Kuhlman-Wilsdorf and Wilsdorf<sup>16</sup> have even suggested that kink bands would not occur in single crystals of this material because the slip lines are too far apart for the dislocations on the corresponding planes to form the necessary kink array.

The second important conclusion reached is that it is the development of multiple systems of slip-band

lamellæ rather than multiple systems of single slip lines which appears to preclude the formation of kink bands. It may be that the effects of grain interaction can be accommodated as effectively by multiple systems of lamellar slip bands as by the formation of kink bands, and that the mechanism which is favoured depends on crystal orientation, the method of deformation, and perhaps on other factors.\* The importance of the development of multiple systems of slip-band lamellæ in precluding kinking is in agreement with the conclusions reached from experiments made with both single-crystal<sup>12,13,19-21</sup> and polycrystalline specimens<sup>13</sup> of pure metals, namely, that "crystals which deform (in tension) from the start in double slip do not develop visible kink bands."<sup>22</sup> The slip referred to is that which can be resolved under the electron microscope as lamellar slip-band clusters<sup>23,24</sup> and which is analogous to the bands responsible for the indications discussed here.<sup>2</sup> It is probable that the "elementary" slip in polycrystalline specimens of the type examined by Honeycombe<sup>13</sup> would have occurred on multiple systems even in those grains in which only single systems of optically detectable bands were observed.<sup>16</sup>

The present results also cast doubts on previous interpretations of the features known as bands of secondary slip. These interpretations have been made on the basis of the distribution of slip-band lamellæ only, and it seems possible that the features could have been associated with kinking on the elementary slip systems. For example, in the field shown in Fig. 7 (Plate LXXI), a prominent, approximately horizontal kink band is apparent in the slip-band indications, and this would be readily detected in the equivalent surface slip traces of lamellar bands on, say, an aluminium crystal. However, the equivalent to the approximately vertical band free from slip-band indications, which is shown from the present work also to be a kink band, presumably would not have contained slip markings and might have been interpreted as a band of secondary slip, particularly since it is almost perpendicular to an obvious kink band. Moreover, the observation frequently made that the primary slip steps do not penetrate into the kink band probably also applies only to bands of lamellar slip. The slip-band indications found in the present specimens usually did not penetrate into the kink bands (Figs. 5-7, Plate LXXI), but, in such cases, the slip-line indications always did so (Fig. 8, Plate LXXI). The inference here is that the justification of the current practice of confining attention to lamellar slip bands when investigating deformation processes, and disregarding the contribution of the "elementary" slip, may require reconsideration.

The development of kink bands in polycrystalline 70 : 30 brass appears to be relatively insensitive to the temperature of deformation, although the bands do become narrower at higher temperatures. In this respect, they differ appreciably from those found by Barrett<sup>9</sup> in  $\beta$ -brass; this further supports Barrett's contention that the decrease in the development of the bands in the latter case may be associated with the ordering of the solid solution. Finally, it is to be noted that the features discussed above do not appear to be associated with those metallographic indications found at compressions above 50% and termed by Samuels<sup>2</sup> "Type IV" or "deforma-

\* As pointed out by Rosi,<sup>25</sup> it then follows that, rather than precluding kinking, the formation of multiple systems of slip bands makes kinking unnecessary.

tion-band" indications; the latter indications are probably associated with deformation bands of another type.

## ACKNOWLEDGEMENTS

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# EFFECTS OF SOLID ENVIRONMENTS ON THE BRITTLE FRACTURE OF ZINC SINGLE CRYSTALS\*

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## SYNOPSIS

It has been found that the normal fracture stress of zinc single crystals oriented with  $\chi_0 = 3^\circ$ , tested in tension at room temperature, is increased 43% upon applying a surface film of copper, gold, zinc oxide, tin, or zinc thicker than about 500 Å. Above this value the increase is independent of film thickness. In addition, the total percentage elongation is increased twofold, the primary mode of deformation being twinning accompanied by parent basal slip both before and after twinning, as well as basal slip within the twins. Metallographic examination reveals a difference in the internal structure of clean and coated crystals, namely the number and distribution of twins. There are more twins in the coated crystals, and they are more uniformly distributed.

In contrast, the fracture stress of coated crystals oriented with  $\chi_0 = 83^\circ$  is 48% less than the value observed with clean-surfaced crystals. The presence of existing twins produced by pre-compression causes the fracture stress of both clean and coated crystals to be increased.

These results, as well as observations on prestrain and recovery, and experiments on film removal, have been explained by a dislocation model in which twins play an important role, by modifying the dislocation path and acting as barriers.

## I.—INTRODUCTION

ALTHOUGH the effects of environment upon the mechanical properties of metals have been investigated, the present paper describes the first comprehensive study of these effects on the brittle fracture of metallic crystals. Roscoe<sup>1</sup> was the first to demonstrate that the strength of crystals is greatly increased by thin surface films of oxide; this observation has been confirmed by other investigators.<sup>2-9</sup> Apart from oxide films, various metallic surface films were observed to strengthen ductile crystals of zinc, tin, and lead, both in tension and in creep.<sup>9-12</sup> Recently, Greenough and Ryder<sup>13</sup> have found that at 77° K. an electrodeposited layer of copper on zinc single crystals oriented with  $20^\circ < \chi_0 < 70^\circ$  caused an approximately twofold increase in the tensile stress necessary to cause cleavage fracture; for a few crystals with  $\chi_0 > 70^\circ$ , the observed cleavage stresses for plated crystals were less than those for unplated ones. They noted that the plastic deformation before fracture was much less for copper-plated than for unplated crystals. In none of these instances can the effects be explained simply by the load-carrying capacity of the film,<sup>1, 11-14</sup> or by residual stresses associated with the film.<sup>10, 14</sup> Dislocation models have been resorted to, in which the film either hinders egress of dislocations and causes a pile-up,<sup>9, 10, 14-16</sup> or it retards the generation of dislocations at the surface,<sup>5, 10, 14, 17</sup> or there is a combination of these two effects.<sup>13</sup>

The present study had two aims: (i) to observe the effects of solid types of environment on the brittle fracture of metallic crystals, and (ii) to develop a model consistent with the observations. For ease of experi-

mentation, zinc single crystals were used, because their ductile → brittle transition temperature in tension, at normal strain rates, lies above room temperature.<sup>18</sup> Crystals with certain orientations were chosen. Those with  $\chi_0 < 5^\circ$  plastically deform on the macroscopic scale only by mechanical twinning; those with  $\chi_0 > 80^\circ$  deform only by slip. One orientation from each group was studied.

## II.—EXPERIMENTAL PROCEDURE

### 1. CRYSTAL PREPARATION

High-purity zinc single crystals were grown by a modified Bridgman technique. Precision-bored Pyrex tubes were used as moulds, and, when filled with polycrystalline zinc of 99.999% purity, were sealed off in a vacuum of  $1 \times 10^{-5}$  mm. of mercury. They were lowered at a rate of 1 in./hr. through a furnace possessing a sharp temperature gradient, and single crystals were thereby produced. These crystals,  $\frac{3}{16}$  in. in dia., were then held in a jig and carefully cut with a jeweller's saw into  $2\frac{1}{2}$ -in. lengths. The Laue back-reflection X-ray method was used to determine crystal orientation, as well as to make sure that the crystals had not been deformed during cutting.

In order to grow a large number of crystals having the desired orientation, a successful seeding technique was developed. The two orientations of seeded zinc single crystals used in this study were  $\chi_0 = 3^\circ$ ,  $\lambda_0 = 28^\circ$  and  $\chi_0 = 83^\circ$ ,  $\lambda_0 = 83^\circ$ ,  $\chi_0$  being the original angle between the basal plane and the specimen axis, and  $\lambda_0$  the original

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angle between the slip direction and the specimen axis. These angles were determined to within  $\pm 1^\circ$ .

## 2. SURFACE PREPARATION

All crystals were cleaned in an 18% nitric acid solution, polished in a chromic acid solution (220 g./l.  $\text{CrO}_3$ , 15 c.c./l.  $\text{H}_2\text{SO}_4$ , and 6 c.c./l. glacial acetic acid), and washed in nitric acid solution, water, and finally alcohol. There was no difference in fracture stress, within the limits of experimental reproducibility, between those polished crystals which were exposed to air for 24 hr. before testing, those tested in air immediately after polishing, and those polished, stored, and tested in an argon atmosphere. Crystals on which this cleaning and polishing procedure was carried out are termed "clean" crystals.

Dense, highly polished, adherent films, 100–35,000 Å. thick, of copper, gold, and zinc were electrodeposited on to clean zinc crystals from cyanide plating baths.<sup>19</sup> Thickness values calculated from Faraday's law, using cathode efficiencies taken from the literature,<sup>19</sup> agreed quite well with the observed weights of the films. The reported film thicknesses were determined with a precision of  $\pm 100$  Å. from the increase in weight on plating, uniformity of coating being assumed. Conventional methods of producing tin films were unsuccessful, but immersion in a solution of 25 g./l.  $\text{SnCl}_3 \cdot 2\text{H}_2\text{O}$ , 12.5 g./l.  $\text{NaOH}$ , and 28 g./l.  $\text{NaCN}$  at about  $85^\circ\text{C}$ . resulted in the formation of tin coatings possessing a silky appearance which seemed quite adherent. By this method quantitative values of the thickness could not be obtained, and the thickness was limited to a maximum of about 2500 Å.

Oxide films 100–7600 Å. thick were produced by heating the crystals in air at  $400^\circ\text{C}$ . for various periods.<sup>20</sup> Sufficiently accurate values of thickness were obtained from data reported in the literature;<sup>20</sup> determination of the small increases in weight due to the films would have required a more sensitive balance than was available.

## 3. TENSILE TESTING

Tensile tests on both clean and coated zinc crystals were carried out in an Instron testing machine at room temperature at a strain rate of  $5 \times 10^{-3}$  sec.<sup>-1</sup> The gripping devices used in the testing of these brittle crystals are described elsewhere.<sup>33</sup> The load at fracture and the total extension were read from automatically recorded load/extension curves. The stress at fracture was calculated from the cross-sectional area of the crystal, obtained from measurements of the diameter to a precision of  $\pm 0.0002$  in. The percentage elongation was calculated from the total extension, with the assumption that end effects in such long specimens are negligible.

The fracture surfaces were approximately perpendicular to the tensile axis. The stress at fracture parallel to the tensile axis, and thus approximately normal to the cleavage surface, has been termed the normal fracture stress,  $\sigma_F$ . The mean value of the normal fracture stresses is designated  $\sigma_{Fm}$  and the limits given for these values represent 95% confidence in the mean. The normal fracture stress can be converted to the resolved normal fracture stress perpendicular to the basal plane by the use of  $\sigma_F$  and the orientation of the

basal plane in the crystal. For the orientation  $\chi_0 = 3^\circ$ , the back-reflection Laue X-ray method and the optical goniometric method showed that the cleavage surface consisted of the prismatic plane in the parent crystal and the basal plane in the twin. The cleavage plane for the orientation  $\chi_0 = 83^\circ$  was identified as the basal plane by means of the back-reflection Laue X-ray method.

## III.—EXPERIMENTAL RESULTS

### 1. BASAL PLANE PARALLEL TO TENSILE AXIS: $\chi_0 = 3^\circ$

#### (a) Effect of Surface Films on Tensile Properties

The mean value of fourteen observations on the normal fracture stress for clean specimens was  $2280 \pm 70$  lb./in.<sup>2</sup>

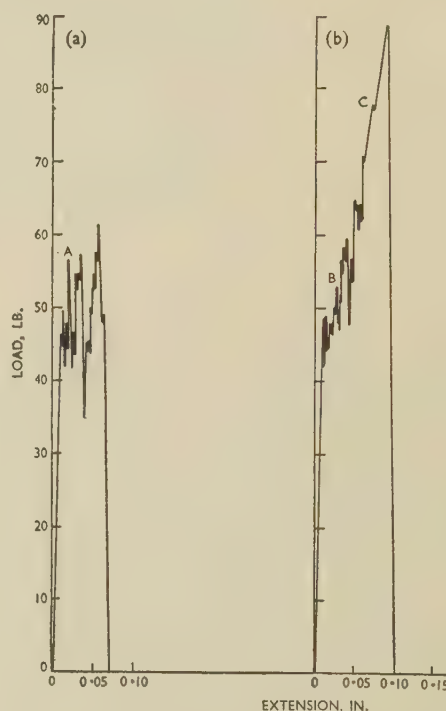


FIG. 1.—Load/Extension Curves of Zinc Single Crystals:  $\chi_0 = 3^\circ$ . (a) Clean crystals; (b) coated crystals.

Although there was some scatter in the results, the reproducibility was considered quite good, in view of the fact that brittle fracture was under investigation. A typical load/extension curve for clean crystals is shown in Fig. 1 (a). The mean value of the percentage elongation before fracture for clean specimens was 2.7%. The fact that single crystals of orientation  $\chi_0 = 3^\circ$  deform extensively by mechanical twinning on the macroscopic scale, is evident from the repeated drops in load. However, there is the possibility that some slip also took place.

The results for crystals with copper films are presented in Fig. 2, in which the normal fracture stress,  $\sigma_F$ , is plotted against film thickness. As in the case of clean crystals, scatter among the data is to be expected. However, the individual values of  $\sigma_F$  fit quite well into a narrow band in the thickness range 500–18,000 Å. and



are independent of film thickness. The mean value of normal fracture stress,  $\sigma_{Fm}$ , was  $3350 \pm 130$  lb./in.<sup>2</sup>, an increase of 47%. For thicknesses less than about 500 Å., only two values were obtained, and in these cases the error was probably large relative to the thickness.

Fig. 1 (b) shows a typical load/extension diagram for a copper-coated specimen (>500 Å.). The mean value of the strain-to-fracture for these specimens was 5.5%—a twofold increase. Up to approximately 3% extension, the diagram was identical with that obtained in testing

curves obtained for the other coatings studied. Therefore a value of  $\sigma_{Fm}$  as well as a value of the fracture strain for tin-coated specimens is included in Table I.

### (b) Effects of Prestrain

A series of experiments was conducted in which clean crystals were prestrained in tension, unloaded, immediately coated with a copper film, and then reloaded to fracture. Although the thickness of the copper film varied, all values lay within the range in which  $\sigma_F$  had

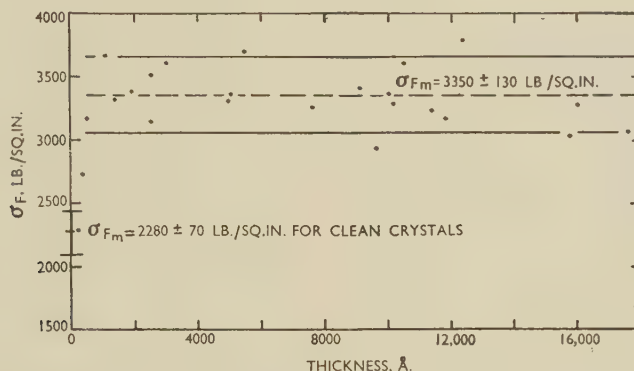


FIG. 2.—Fracture Stress Plotted Against Thickness of Copper Coating for Zinc Single Crystals:  $\chi_0 = 3^\circ$ .

clean crystals. The remaining strain was accompanied by a great amount of strain-hardening. From such diagrams, it was difficult to ascertain whether this last stage of extension was due primarily to slip or to further twinning. To determine this, copper-coated crystals were tested at a strain rate of  $5 \times 10^{-5}$  sec.<sup>-1</sup>, i.e. one hundred times as slow as the normal strain rate used. From the resulting load/extension curves, it was observed that this latter portion of the elongation consisted of small jogs characteristic of twinning. At the normal strain rate, the recording pen was unable to follow these small jogs, and consequently a smooth curve was obtained in the latter stages of strain. The high rate of strain-hardening is probably to be explained by the rapid decrease of available volume within which each new twin must form.

Gold, zinc oxide, and zinc films on crystals of orientation  $\chi_0 = 3^\circ$  produced effects identical with those

previously been observed to be independent of thickness. The results of these experiments are shown in Fig. 3, where normal fracture stress is plotted against percentage prestrain. Extrapolation of the band to the mean value of strain observed in clean crystals, 2.7%, gave a range of values of  $\sigma_F$  which contained the experimentally observed value of  $\sigma_{Fm}$  for clean crystals

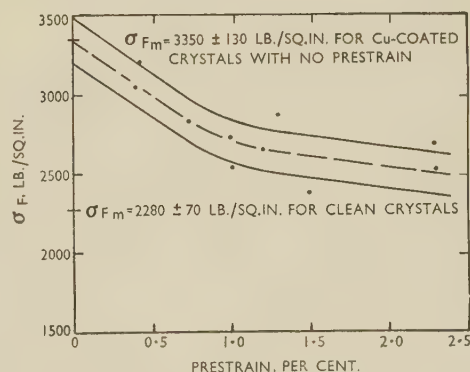


FIG. 3.—Effect of Prestrain on Copper-Coated Zinc Single Crystals:  $\chi_0 = 3^\circ$ .

TABLE I.—Effects of Surface Films on Tensile Properties of Zinc Single Crystals:  $\chi_0 = 3^\circ$ .

Surface Film	Mean Total Elongation, %	$\sigma_{Fm}$ , lb./in. <sup>2</sup>
Clean . . . . .	2.7	$2280 \pm 70$
Copper . . . . .	5.5	$3350 \pm 130$
Gold . . . . .	5.6	$3165 \pm 95$
Zinc oxide . . . . .	5.1	$3170 \pm 155$
Zinc . . . . .	5.5	$3320 \pm 145$
Tin . . . . .	5.8	$3225 \pm 190$

observed on copper coatings. The values of  $\sigma_{Fm}$  and the mean value of fracture strain observed for these films are presented in Table I. Although thickness of tin films could not be determined, the plot of  $\sigma_F$  against immersion time was very similar to the  $\sigma_F$ /film-thickness

( $2280 \pm 70$  lb./in.<sup>2</sup>). Application of a surface film after prestraining an initially clean specimen to a point immediately preceding fracture does not, therefore, increase its normal fracture stress. In addition, the total amount of elongation (prestrain + strain observed in final testing) decreased, as did  $\sigma_F$ , in this series of tests.

### (c) Effects of Recovery

A series of experiments on recovery was performed, as the time between prestraining and final loading might be sufficient to permit recovery to take place in zinc crystals

at room temperature. Heat-treatments of 26 hr. at room temperature and 19 hr. at 70°C. were used to produce recovery. The measure of the degree of recovery was the amount by which the yield point decreased with time, relative to the amount that it had been raised by straining. The positions on the load/extension curves where the crystals were allowed to recover are marked in Figs. 1 (a) and 1 (b) for clean and coated crystals, respectively. The results of these tests are given in Table II.

Recovery had no effect on the value of  $\sigma_F$  for clean

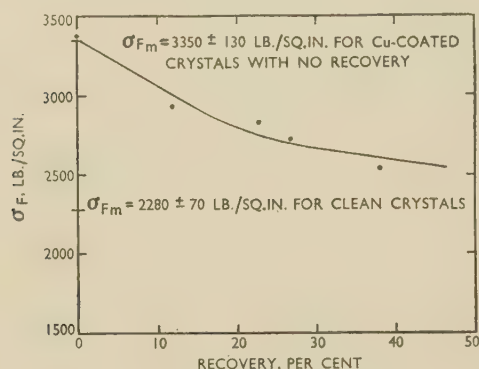


FIG. 4.—Effect of Recovery on Copper-Coated Zinc Single Crystals:  $\chi_0 = 3^\circ$ . Interrupted at B (see Fig. 1 (b)) for recovery.

crystals which recovered at position A in Fig. 1 (a), nor on copper-coated specimens which recovered after about 5.0% strain (position C in Fig. 1 (b)). However, both the normal fracture stress and the total elongation of copper-coated specimens which recovered after about

TABLE II.—Effect of Recovery on Copper-Coated Zinc Single Crystals:  $\chi_0 = 3^\circ$ .

Thickness of Cu Film, Å.	Position Interrupted (see Fig. 1)	Recovery, %	Elongation, %	$\sigma_F$ , lb./in. <sup>2</sup>
...	A	36	3.0	2290
1900	B	0	5.3	3380
2400	B	12	5.0	2930
3700	B	23	4.3	2830
3500	B	27	4.8	2720
4500	B	38	3.8	2530
2400	C	11	6.0	3295
3800	C	20	7.0	3665
3700	C	27	6.0	3325

2.3% strain (position B in Fig. 1 (b)) were affected. The data for specimens in this latter case are plotted as values of  $\sigma_F$  against percentage recovery in Fig. 4. This curve is of the same shape as the curve obtained in prestrain experiments, and extrapolation to 100% recovery again gives the  $\sigma_{Fm}$  value for clean crystals.

#### (d) Effects of Removing the Film

In order to determine whether the surface film caused these effects directly, or whether the film in some way produced changes in the internal structure of the crystals, which in turn produced these effects, a series of

experiments was carried out in which copper-coated crystals were loaded, the loading interrupted, the surface film immediately removed, and finally the crystals were reloaded to fracture. All coatings were between 2200 and 2500 Å. thick. The results observed are presented in Table III. For those specimens from

TABLE III.—Effect of Removing Film from Copper-Coated Zinc Single Crystals:  $\chi_0 = 3^\circ$ .

Elongation, Before Removal, %	Total Elongation, %	$\sigma_F$ , lb./in. <sup>2</sup>
1.7	3.1	2365
2.0	3.7	2620
2.1	3.4	2370
2.4	3.7	2340
2.9	3.9	2625
3.1	6.7	3985
3.3	6.7	4265
3.8	6.0	3395
3.9	5.2	3525
4.2	5.2	3195
4.7	5.4	3285
4.9	5.5	3045
5.0	5.7	3290
5.0	5.5	3120

which the surface film was removed before the elongation had reached about 3.0%, the normal fracture stress was essentially the same as that observed for clean specimens. Therefore, during the first 3.0% strain the presence of a surface film did not contribute at all to the increase of  $\sigma_F$ . For crystals from which the film was removed when the elongation was between 3.0 and 5.0%, however, the normal fracture stress was the same as though the film were present throughout the whole test. These observations indicate that the surface film does not directly cause an increase in  $\sigma_F$ , but rather that it alters the internal structure of the crystals in such a manner as to induce this effect.

#### (e) Metallographic Studies

Cross-sectional areas away from the fracture surfaces of both clean and coated specimens were studied, after examination of the fracture surfaces themselves had revealed clustering of twin bands in the case of clean crystals. Specimens were carefully cut with a jeweller's saw, etched with an 18% nitric acid solution to remove any traces of cold working, and finally polished and etched with a chromic acid solution in preparation for microscopic examination. The twins in the cross-section of the coated crystals were quite uniformly distributed over the whole area; in the clean crystals, the twins appeared in clusters with large distances between such clusters. In addition, many more twin bands were present in the coated crystals than in the clean ones. The mean distance between twin bands in the coated crystals and the mean distance between clusters in the uncoated were measured. These two mean values, 0.18 mm. and 0.56 mm. respectively, represented the average maximum distances between twin bands in the cross-sectional areas. When these mean values were resolved into the direction of slip they were found to be 0.38 mm. and 1.19 mm., respectively. Twin distribution in the



longitudinal direction also was examined (Figs. 6 (a) and (b), Plate LXXIII), and, as in the cross-sectional areas, a pronounced clustering effect was observed in clean specimens, whereas coated crystals showed a uniform distribution of twins. In addition, twinning had occurred on a second system to a great extent in coated crystals but to a limited extent in clean specimens. Therefore a difference in the internal structure between clean and coated crystals was experimentally observed, namely the number and distribution of twins.

Although the primary mode of deformation in single crystals of this orientation is mechanical twinning, the occurrence of slip was also investigated. Clean crystals were loaded to a point just before the first indication of twinning was observed and were examined in the unetched condition. No twin bands were present, but parallel lines which disappeared upon etching were observed in the longitudinal direction on the surfaces of the specimens (Fig. 7 (a), Plate LXXIII). Specimens examined before any load was applied did not contain these lines, and final confirmation that the lines were traces of basal (0001) slip was provided by stereographic analysis. Clean crystals strained in the twinning region of the load/extension diagram also showed parent basal slip lines on the surface (Fig. 7 (b), Plate LXXIII). These lines appeared much stronger than in the preceding case, indicating that more basal glide took place after twinning had started. Occasionally, basal glide in the twins also was observed. Copper-coated crystals strained and examined for evidence of slip gave similar results (Figs. 8 (a) and (b), Plate LXXIII). However, for a given amount of strain, there were fewer and better-defined slip lines in the clean crystals than in the coated ones, evidence that slip took place on more slip planes in crystals with surface films.

It can therefore be concluded that although mechanical twinning was the principal mode of plastic deformation in zinc single crystals of orientation  $\chi_0 = 3^\circ$ , basal slip did occur both in the parent crystal before and after twinning and in the twin bands after the reorientation of the basal planes by twinning. The occurrence also of parent basal slip before twinning has been recorded by Bell<sup>21</sup> in his work on zinc single crystals of orientations similar to those used in the present study. In addition, he observed non-basal glide, (11 $\bar{2}$ 2), in the parent crystal before the onset of twinning; this parent pyramidal slip was not observed in the present investigation.

## 2. BASAL PLANE PERPENDICULAR TO TENSILE AXIS :

$$\chi_0 = 83^\circ$$

### (a) Effects of Surface Films on Tensile Properties

Zinc single crystals of orientation  $\chi_0 = 83^\circ$  fractured in a brittle manner at room temperature with no observed prior plastic strain. Sixteen specimens were tested, and a value of  $1160 \pm 180$  lb./in.<sup>2</sup> was found for  $\sigma_{F_m}$ . Although no strain was observed, microscopic examination revealed slip lines which, as stereographic analysis confirmed, were due to basal glide. There was no microscopic evidence of twinning.

Since all surface films used with zinc crystals of orientation  $\chi_0 = 3^\circ$  gave identical results, copper was selected as a representative surface coating in studying specimens of orientation  $\chi_0 = 83^\circ$ . Basal slip with no

twinning was found upon microscopic examination. The normal fracture stress proved to be independent of film thickness in the whole range studied (100–9600 Å.), and  $\sigma_{F_m}$  was observed to be  $605 \pm 120$  lb./in.<sup>2</sup>, a decrease of 48% from the value obtained with clean crystals. Greenough and Ryder<sup>13</sup> observed this decrease, but were sceptical of it on account of the exacting testing techniques required and the small number of crystals tested.

### (b) Effects of Precompression

When crystals of orientation  $\chi_0 = 83^\circ$  are compressed, the plastic strain is primarily manifested as twinning, so that this series of experiments was in reality an investigation of crystals having pre-existing twins. The pre-compression used varied from about 0.5 to 1.5%. In this range, the normal fracture stress was independent of the amount of precompression, and  $\sigma_{F_m}$  was found to be  $1600 \pm 180$  lb./in.<sup>2</sup> for clean specimens, copper-coated specimens, and crystals coated with a copper surface film after precompression. Hence, regardless of whether or not the crystal had a surface film,  $\sigma_{F_m}$  increased to the same stress level. Again, the presence of twin bands increased the fracture stress.

## IV.—DISCUSSION OF RESULTS

None of the models proposed to interpret similar experiments is found to be consistent with the present authors' observations, especially since the fracture stress was increased upon application of a surface film to the crystals of one orientation studied ( $\chi_0 = 3^\circ$ ), whereas a decrease in fracture strength was obtained in crystals of the other ( $\chi_0 = 83^\circ$ ). A satisfactory model must also resolve the difference between the low brittle fracture strength and the theoretical value of the cohesive strength; for zinc, the ratio of these is of an order of magnitude between 10 and 100.<sup>22, 23</sup> Since the assumption of pre-existing cracks in metals, used successfully by Griffith in his theory of brittle fracture of glass,<sup>24</sup> has been objected to on theoretical grounds,<sup>25</sup> it becomes necessary to ascertain the origin of cracks which subsequently lead to brittle fracture.

A dislocation theory of fracture has been advanced,<sup>26–30</sup> in which the local high stress concentrations—greater than the theoretical cohesive strength of the material—result from pile-ups of dislocations at barriers. The number of dislocations in an array of like dislocations piled up at a barrier under an applied shear stress, has been calculated by Eshelby, Frank, and Nabarro<sup>31</sup> to be :

$$n = L\tau/2D \quad . \quad . \quad . \quad (1)$$

where  $L$  is the length of slip plane between the source and the barrier,  $\tau$  is the applied shear stress, and  $D = Gb/2\pi(1 - \nu)$ , in which  $G$ ,  $b$ , and  $\nu$  are the rigidity modulus, Burgers vector, and Poisson's ratio, respectively. Koehler<sup>32</sup> has calculated the large tensile stresses set up, and from this calculation, Greenwood and Quarrell<sup>26</sup> have postulated that the criterion for brittle fracture is :

$$\sigma = kn\tau \geq \sigma_{l.c.s.} \quad . \quad . \quad . \quad (2)$$



where  $\sigma_{t.c.s.}$  is the theoretical cohesive strength of the material, and  $k$  a constant of the order of unity. Substituting the value of  $n$  from equation (1) gives:

$$\sigma = kL\tau^2/2D \geq \sigma_{t.c.s.} \quad . \quad . \quad . \quad (3)$$

This analysis has been used successfully to account for experimental observations on polycrystalline zinc<sup>26</sup> and on single crystals of iron.<sup>33</sup> Grain boundaries were regarded as the barriers in the polycrystalline zinc, and twin bands as the barriers in iron single crystals tested at low temperatures. In both cases, the number of piled-up dislocations required to cause fracture was found to be of the order of  $10^3$ .

Stroh<sup>28</sup> also has calculated the maximum tensile stress due to a pile-up. Upon equating this with the Griffith condition that a crack is accompanied by a decrease in energy of the system, Stroh has postulated the criterion for fracture to be:

$$n\tau \geq 12\alpha G \quad . \quad . \quad . \quad (4)$$

where  $\alpha = \gamma/Gb$ ,  $\gamma$  being the surface energy. Substituting the value of  $n$  from equation (1) gives:

$$\frac{L\tau^2}{2D} \geq 12\alpha G \quad . \quad . \quad . \quad (5)$$

Comparison of equation (5) with equation (3) shows that the left-hand sides are nearly identical, since  $k$  is approximately unity and the one equation would reduce to the other if  $\sigma_{t.c.s.} = 12\alpha G$ . Stroh<sup>28</sup> has estimated  $12\alpha G$  to be  $0.7G$ , and this compares favourably with other estimates of theoretical cohesive strength, including Orowan's estimate of  $0.1G$ .<sup>28</sup>

From this analysis of brittle fracture, it is seen that the shorter the length of slip plane  $L$ , the greater the fracture stress; conversely, a greater length of slip plane, on which more dislocations can be held up, will cause the fracture stress to decrease. Let us apply this criterion to zinc single crystals oriented with  $\chi_0 = 3^\circ$ , and let us consider that twin bands act as barriers for dislocation pile-ups. Then  $L$  can be replaced by  $T$ , the mean maximum distance between twins resolved in the slip direction, and it is seen from the measured values of  $T$  that the fracture stress of the coated crystals should be greater than that of clean specimens.

Coated specimens of this orientation, the films on which were removed before 3.0% strain had been reached, fractured at the same stress level as clean crystals. This indicated that  $T$  was not changed significantly by the presence of a surface film up to this value of strain. However, coated crystals from which the film was removed when elongation exceeded 3.0% fractured at a stress equivalent to that found for crystals on which a film remained throughout the entire test. Therefore, the change in  $T$  took place at about 3% strain. The problem is to explain how the surface film causes this change in twin distribution.

Reviewers<sup>34,35</sup> of the numerous investigations carried out to determine the critical stress of twinning have concluded that this process is one of nucleation and growth, the nucleation stress level being higher than the subsequent growth stress. Hall<sup>35</sup> suggests a few possible modes of nucleation, one of which is by twin dislocations.

These may be initially present in the crystal and/or may be formed by means of stress concentrations that develop around arrays of slip dislocations held up by a barrier. Other suggested mechanisms are nucleation by slip-dislocation interaction and nucleation by elastic strains. The model involving twin dislocations formed by slip-dislocation pile-ups can be utilized to explain the change in  $T$  due to surface films. Whereas dislocations associated with basal glide are free to pass out of a crystal having a clean surface, a surface film will act as a barrier and the majority of dislocations will be held up. Furthermore, this pile-up creates a back stress that prevents further generation and movement of dislocations along this particular slip plane and other planes immediately adjacent. Slip or movement of dislocations can now occur on other planes. Thus, for a constant value of strain, dislocations are confined to fewer slip planes in clean crystals than in coated ones, as was observed in the present work.

Because of the greater number of active slip planes existing in coated crystals, the dislocation pile-ups should involve fewer dislocations than are required for fracture, and the stress concentration arising from these will lead to the formation of the twin dislocations which, in conjunction with the applied stress, produce twin nuclei. Observations of the longitudinal twin distributions revealed twinning on a second system to a much greater extent in the coated specimens than in the clean ones, and it is thought that the formation of these twin nuclei and their subsequent growth occur primarily on the second system. It is to be expected that the stresses, both of nucleation and of growth, associated with the second twin system will be greater than on the primary system, and it seems that the stress required for the formation of twin nuclei on the second system is reached at 3.0% strain. Comparison of the load/extension curves for clean and coated specimens (Figs. 1 (a) and (b)) shows that the curves are identical up to about 3.0% strain. With coated crystals, the remaining portion of the diagram is composed of small jogs, indicative of the formation of small twins which microscopic examination shows to be predominantly on the second system. Above a certain thickness, the surface film will reach its limit as an effective barrier, and thus, as was observed, the effects of surface films on  $\sigma_F$  will be independent of the thickness as well as of the material of the film.

From the results of the tests involving prestrain, it is to be expected that the greater the amount of prestrain before the surface film is applied, the more dislocations due to basal slip will pass out of the crystal. This will result in the number of twin nuclei that can be formed after the film is present being smaller, and this in turn will lead to a larger value of  $T$  and, therefore, a smaller increase in  $\sigma_F$  due to the presence of the surface film.

In those coated specimens strained to about 5.0% before recovery,  $T$  had already been altered to what was essentially its final value; thus, no change in normal fracture stress due to recovery was to be expected. For coated crystals strained about 2.0% before recovery, small dislocation pile-ups are expected to be present, but new twins have not formed. Since it has been associated with the annihilation of unlike dislocations as well as with the redistribution of dislocations in the matrix,<sup>36</sup> recovery will decrease the number of dislocation pile-ups,



and therefore increasing amounts of recovery will result in smaller increases in  $\sigma_F$  due to the presence of surface films.

In crystals from which the film is removed after about 3.0% strain,  $T$  is altered to its final value, and the fracture stress will be independent of whether or not the surface coating is present throughout the remainder of the test. On the other hand, the removal of the film before 3.0% elongation has been reached will allow dislocations piled up at the film to move out of the crystal, twin nuclei due to these pile-ups will not form, and upon further loading the specimens will behave in the same way as initially clean crystals.

The remaining observations to be accounted for by this model are those made on crystals oriented with  $\chi_0 = 83^\circ$ . Again, the fracture stress is dependent on the number of dislocations that pile up at a barrier. For this orientation, twinning does not occur and the picture becomes simplified. On the assumption that in the absence of twins the crystal surface almost always acts as the most effective barrier (fracture nearly always starts at the surface), but that in clean crystals this surface barrier is less effective than when a coating is present, surface films should always result in greater dislocation pile-ups and lower values of the fracture stress. Moreover,  $\sigma_F$  will not depend on the thickness of the film once it is sufficiently thick to act as an effective barrier. When twins were introduced by means of precompression,  $\sigma_F$  was increased to the same value for both clean and coated specimens. This is to be expected, since  $L$  was reduced to the same value and the number of dislocations piling up at barriers and raising the fracture stress was decreased.

The number of dislocations that piled up at a barrier at fracture and the stress concentrations arising from these pile-ups were calculated for both clean and coated crystals oriented with  $\chi_0 = 3^\circ$  and coated crystals oriented with  $\chi_0 = 83^\circ$ . No values could be obtained for clean crystals of the latter orientation, since equation (1) is not applicable owing to the absence of completely effective barriers. The calculated values are :

Crystals	$n$	$\sigma$ , dynes/cm. <sup>2</sup>
$\chi_0 = 3^\circ$ ; clean	330	$2.4 \times 10^9$
$\chi_0 = 3^\circ$ ; coated	295	$3.1 \times 10^9$
$\chi_0 = 83^\circ$ ; coated	280	$1.4 \times 10^9$

These values were determined by using values of  $3.8 \times 10^{11}$  dynes/cm.<sup>2</sup> for the rigidity modulus,  $12.7 \times 10^{-8}$  cm. for the Burgers vector, and 0.2 for Poisson's ratio. The slip length,  $L$ , was replaced by  $T$  in the case of crystals oriented with  $\chi_0 = 3^\circ$ , and one-half the diameter of the specimens was used as the value for  $L$  in crystals oriented with  $\chi_0 = 83^\circ$ . In calculating  $\tau$  (the applied shear stress) for crystals oriented with  $\chi_0 = 3^\circ$ , it was assumed that the stress was uniformly distributed in spite of the twinning. These values are of at least one order of magnitude lower than the values usually assigned to the cohesive strength, two orders of magnitude lower than that calculated by Stroh<sup>28</sup> from the modified Griffith theory (equation (4)), and up to one order of magnitude lower than would be obtained from an analysis by Stroh<sup>29</sup> in which he pointed out that pile-ups on neighbouring slip planes can become a co-operative phenomenon and that thereby individual stress concentrations are additive.

Petch<sup>27, 37</sup> has arrived at a relationship between brittle fracture stress,  $\sigma_F$ , and grain diameter,  $d$ , namely :

$$\sigma_F = \sigma_0 + Kd^{-\frac{1}{2}} \quad (6)$$

in which  $\sigma_0$  and  $K$  are constants. This relationship fully satisfied his experimental observations on ferrites,<sup>37</sup> as well as the results obtained on polycrystalline zinc by Petch<sup>27</sup> and by Greenwood and Quarrell.<sup>26</sup> Stroh,<sup>30</sup> on purely theoretical grounds, has also derived a linear relationship between fracture stress and the reciprocal of the square root of the grain diameter, in which  $d = 2L$ . This relationship is expressed as follows :

$$\sigma_F d^{\frac{1}{2}} = 4[6\gamma G/\pi(1-v)]^{\frac{1}{2}} = 1.2 \times 10^8 \text{ (dynes/cm.}^2\text{)cm.}^{\frac{1}{2}} \quad (7)$$

By putting  $d = 2T$  for crystals oriented with  $\chi_0 = 3^\circ$  and  $d$  = specimen diameter, the values of  $\sigma_F d^{\frac{1}{2}}$  have

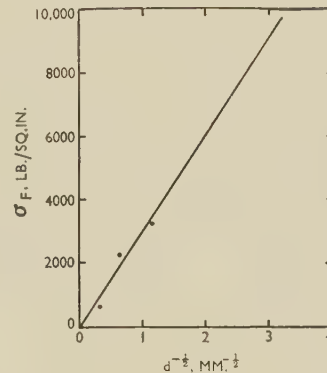


FIG. 5.— $\sigma_F$  Plotted Against  $d^{-\frac{1}{2}}$  for Zinc Single Crystals.

been calculated for the orientation  $\chi_0 = 83^\circ$ , and are listed below :

Crystals	$\sigma_F d^{\frac{1}{2}}$ (dynes/cm. <sup>2</sup> )cm. <sup>1/2</sup>
$\chi_0 = 3^\circ$ ; clean	$7.7 \times 10^7$
$\chi_0 = 3^\circ$ ; coated	$6.3 \times 10^7$
$\chi_0 = 83^\circ$ ; coated	$2.9 \times 10^7$

These values compare very favourably with the values  $1 \times 10^8$  and  $5.7 \times 10^7$  obtained with brittle polycrystalline zinc tested at  $-196^\circ$  C. by Greenwood and Quarrell<sup>26</sup> and by Petch,<sup>27</sup> respectively. In addition, a plot of  $\sigma_F$  against  $d^{-\frac{1}{2}}$ , as shown in Fig. 5, resulted in a straight line passing through the origin. This straight-line relationship in Fig. 5 is represented by the equation  $\sigma_F = 3000 d^{-\frac{1}{2}}$ , whereas those observed by Greenwood and Quarrell<sup>26</sup> and by Petch<sup>27</sup> on polycrystalline zinc at  $-196^\circ$  C. were, respectively,  $\sigma_F = 4700 d^{-\frac{1}{2}}$  and  $\sigma_F = 500 + 2600 d^{-\frac{1}{2}}$ . Thus a straight-line relationship between fracture stress and available length of slip plane, very similar to the straight-line dependency of fracture stress on grain diameter for polycrystalline material, has been observed with zinc single crystals.

## V.—CONCLUSIONS

- (1) Surface coatings affect fracture stress.
- (2) The dislocation-pile-up-at-a-barrier model adequately describes the effects observed.
- (3) Twins play an important role in this process by modifying the dislocation path and acting as barriers.

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# SOLID-SOLUTION HARDENING OF ALUMINIUM AND MAGNESIUM \*

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## SYNOPSIS

A linear relation between concentration and extent of hardening has been observed for various solutes dissolved in aluminium and magnesium. A relationship also exists between hardening and the distortion introduced into the lattice by the solute; with certain exceptions, this relationship takes a linear form with aluminium and a quadratic form with magnesium. The results are in reasonable agreement with the predictions of Mott and Nabarro (*Rep. Conf. on Strength of Solids*, (*Phys. Soc.*), 1948, p. 1), whose approach is considered likely to prove of greatest value to the metallurgist interested in alloy development.

## I.—INTRODUCTION

It is generally acknowledged that the mechanical strength of metals is improved by the presence of other elements in solid solution, and indeed this is probably one of the principal objects of alloying. Attempts to explain the fact that a metal is almost invariably hardened by the addition of a second element, even when the latter is softer than the parent metal, have lagged behind the application of the principle, with the result that the development of high-strength alloys has not always been as systematic as it might have been. More recently, however, the subject has received considerable attention, and published information may be conveniently divided into two groups: one in which the emphasis has been placed on the experimental determination of what may be regarded as empirical relationships, and a second in which the approach has been theoretical and based upon the properties of dislocations.

Most of the experimental studies have used hardness measurements as a convenient method of assessing the resistance of a material to deformation, although more recently yield-strength measurements have been employed. Goebel<sup>1</sup> was one of the early workers who systematically studied the change in hardness caused by alloying, by the addition of various solutes to lead. This work was soon followed by that of Norbury<sup>2-4</sup> on solid solutions of copper, as a result of which a linear relationship was observed between the hardening effect of a solute and the change in mean atomic volume on alloying. Norbury therefore postulated that the hardness of simple substitutional solid solutions was generally proportional to the difference in atomic size of the solute and solvent, but that exceptions due to "chemical-affinity" effects may be observed, as in the cases of silicon dissolved in copper and sodium in lead. Brick, Martin, and Angier<sup>5</sup> obtained a considerable degree of confirmation of Norbury's work on copper primary solid solutions. They observed that the degree of hardening produced by various solutes depended primarily on the difference in atomic volume of solute and solvent or, relatedly, on the parameter change of the solvent or the extent of solid solubility.

Several refinements to these relationships resulted from the work of Frye and Hume-Rothery<sup>6</sup> on solutions of eight different elements in silver, which revealed a closely linear dependence of hardness increment on the square of the lattice-parameter change when the dissolved atoms belonged to the same row of the Periodic Table and were present in the same amounts. These results were supported by those of Frye and Caum<sup>7</sup> on copper solutions containing the elements Zn, Ga, Ge, and As, from the same row of the Periodic Table as the solvent. Shortly afterwards, Frye, Caum, and Treco<sup>8</sup> subjected the aforementioned results on analogous copper and silver solid solutions to a mathematical treatment. After attempting to allow for the possible influence of ionic overlap, they obtained a linear relationship between hardness increase and the calculated increase in lattice stress when zinc dissolved in copper is replaced by Ga, Ge, or As, and when cadmium dissolved in silver is replaced by In, Sn, or Sb.

More recent work by French and Hibbard<sup>9</sup> on the yield strengths and Vickers pyramid hardness of copper solutions containing Si, Ni, Al, Zn, Be, Cd, and Sn indicates an approximate relationship between yield strength (or hardness) and lattice-parameter change, despite the fact that the solutes are randomly situated in the Periodic Table. An absence of dependence on position in the Periodic Table was likewise observed by Meyer<sup>10</sup> in investigating the hardening of nickel by eleven different solutes. Hardness appeared to be a linear function of atomic concentration throughout the temperature range  $-183^{\circ}$  to  $300^{\circ}$  C., except in the case of solutions containing Sn, Si, or Sb. There was only a slight degree of scatter when values of hardness increment for the various solutes were plotted against the lattice strain they produced. Although again all the solute elements were not chosen from the same row of the Periodic Table as the solvent, solutions of Mn, Ni, Cr, Co, Mo, or Si in iron showed a similar relationship between hardness increment and lattice-parameter change. When the Vickers hardness values obtained by Austin<sup>11</sup> are plotted against the lattice distortion per atomic per cent., they are found to lie closely about a straight line except in the case of chromium and cobalt. Austin

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himself pointed out that the hardening effect was proportional to the difference in atomic radius between the added element and pure iron, and also depended on the structural type of the added element. The deviation in the case of cobalt is especially remarkable, since it represents a hardening effect in the almost complete absence of lattice distortion. Further research into the plastic properties of ferritic materials was conducted by Lacey and Gensamer,<sup>12</sup> who found that the strengthening was a parabolic function of solute concentration, the coefficient of proportionality depending on the solubility of the element concerned. They found that this did not apply to solutions of silicon or cobalt.

Some similarity is apparent between the case of cobalt dissolved in iron and silver in aluminium. Although the addition of silver produces negligible change in the lattice parameter of aluminium, nevertheless it was found by Dorn, Pietrowsky, and Tietz<sup>13</sup> to cause considerable increase in the flow stress and the rate of strain-hardening. These workers investigated the tensile properties of aluminium solid solutions in relation to changes in lattice parameter. They repudiated the earlier inference that there was a factor associated with the atomic period of the solute element and proposed that it was more likely to be connected with the conditions of metallic bonding. This valency factor was considered responsible for the solution-hardening effect of silver, but calculations based on this supposition necessitated a valency of 2 electrons per atom in aluminium.

Allen, Schofield, and Tate,<sup>14</sup> working with  $\alpha$  solid solutions of copper, confirmed the operation of a valency factor in the hardening process. Since solvent and solutes all belonged to the same row of the Periodic Table, they all had the same ionic core. The ultimate tensile strength and the resistance to plastic deformation appeared to be almost entirely governed by the electron:atom ratio of the alloys. Work by one of the present authors (D. H.) on this series of alloys showed that both the "annealed hardness" and the rate of work-hardening were related to the electron concentration in the alloy.

As early as 1921, Rosenhain<sup>15</sup> had suggested that solid-solution hardening was due to the solute atoms causing disturbances in the slip planes, but it is only in the last ten years that attempts have been made to derive quantitative relationships based upon this idea. This has largely been the work of Mott and Nabarro<sup>16-18</sup> and has resulted in the derivation of relationships for the stress necessary to promote movement of a flexible dislocation line when opposed by internal stresses resulting from the misfit of the solute atoms on the solvent lattice. Slightly different treatments of the problem yield varying results as to the degree of dependence of the yield strength on the lattice distortion, but the theory indicates that the hardening should be a linear function of the concentration of solute and a quadratic or lesser function of distortion, according to the estimate of the length of dislocation which moves as a coherent piece. The theory is in agreement with experiment to a certain extent,<sup>17</sup> but clearly cannot account for those chemical or valency effects previously mentioned.

The Mott and Nabarro treatment is based on the assumption that the solute atoms are randomly distributed on the lattice of the solvent metal, but it is well

known that most solid solutions show some degree of clustering or short-range order. Clearly, the interaction of such regions with dislocations will be different from that due to single solute atoms, and so the strength of a solid solution may be expected to be dependent upon the dispersion of the dissolved atoms. Detailed consideration indicates that there are a number of ways in which solute atoms can react with dislocations and, therefore, presumably influence the strengthening effect due to alloying. Thus, Cottrell<sup>19</sup> has developed the idea that solute atoms will form an atmosphere around dislocations in a body-centred cubic lattice, because of the compatibility of the lattice strains. It follows then that, if the dislocation is to move, extra force must be applied in order to free it from its atmosphere of solute atoms. Suzuki<sup>20</sup> has shown how a similar mechanism can operate in the case of face-centred cubic and close-packed hexagonal lattices, by the collection of solute atoms in extended dislocations. In these cases the segregation of the solute atoms is likely to be the result of chemical, rather than volumetric, interaction between the atoms. Fisher<sup>21</sup> has also pointed out that in those solid solutions where the solute atoms are not randomly dispersed, i.e. where clustering or short-range order exists, there will be an appreciable contribution to strength by virtue of the fact that the passage of a dislocation through such regions will alter the equilibrium dispersion.

With the advent of these refinements of the model used by Mott and Nabarro to explain solid-solution hardening in terms of dislocation theory, some authors have considered the original ideas to be invalid and, by inference, the theory to be untenable. It would appear, however, that a more reasonable view would be that the work of Mott and Nabarro gives an acceptable generalized result and that subsequent developments are of value in explaining specific cases.

## II.—EXPERIMENTAL PROCEDURE

### 1. ALUMINIUM SOLID SOLUTIONS

Materials of high purity were used for the preparation of binary solid solutions containing Cu (99.96%), Ge (99.99%), Mg (99.95%), Ag (99.99%), Zn (99.99%), or Si. The aluminium was 99.992% pure and the silicon was introduced in the form of a high-purity hardener alloy containing 12.23% Si and 87.74% Al.

Extreme care was taken during melting and subsequent treatment to prevent the introduction of impurities. In general, alloys were melted in Salamander crucibles in a gas-fired furnace with a standard protective flux. No degassing was carried out, but the gas content was kept to a minimum by preheating the charge and the avoidance of overheating after melting. Ingots  $1\frac{1}{2}$  in. in dia.  $\times$   $3\frac{3}{8}$  in. long were cast in preheated graphite moulds. The alloys containing germanium were prepared as ingots 1 in. dia.  $\times$   $1\frac{1}{2}$  in. long by melting in alumina crucibles in an electric furnace. The outer surfaces of the ingots were removed by machining, and the ingots were then homogenized by annealing for 5 days at a convenient temperature within the solid-solution range. Contamination during this treatment was prevented by sealing the ingots in Pyrex glass tubes packed with



carbon granules. The annealed ingots were subsequently reduced to  $\frac{1}{2}$ -in.-dia. rod by a combination of hot rolling, or extrusion, and cold rolling. The latter was employed as a finishing process to introduce sufficient work-hardening to induce recrystallization on subsequent annealing. The reason for this was that at first it was considered essential to conduct hardness tests on specimens of various grain-sizes and so enable all results to be related to a standard grain-size. Specimens about  $\frac{1}{2}$  in. deep, cut from the alloy rods, were annealed, protected by carbon granules or an alumina boat, to promote recrystallization and grain growth. Different grain-sizes were obtained by varying the temperature of treatment or, alternatively, the annealing time. Temperatures were chosen within the range of complete solubility, and solutions were retained by subsequent quenching in water. Hardness testing was carried out immediately after quenching, precautions being taken to ensure that age-hardening effects were absent.

Meyer hardness analyses were used throughout the work, the hardness values being expressed as "ultimate ball numbers" ( $Pu$ ), i.e. the value which the mean pressure attains when the ball is forced into a material to its equator and the impression diameter becomes equal to the ball diameter. Thus:

$$Pu = 4aD^{n-2}/\pi,$$

where  $D$  is the ball diameter and  $a$  and  $n$  are the constants in the equation

$$L = ad^n,$$

representing the relationship between the applied load,  $L$ , and the impression diameter,  $d$ . A Meyer analysis enables the values of  $a$  and  $n$  to be determined by measuring the impression diameters corresponding to at least two loads, although O'Neill<sup>22</sup> advises the use of at least three and preferably four loads covering not less than a 3:1 ratio. In the present work, six loads varying from 5 to 30 kg. were generally employed. The "method of concentric impressions", involving successive loadings of the ball to higher pressures in a previously measured indentation, was used, as this reduces the surface area required for tests and, in addition, gives a whole series of values at each of several points, thus allowing detection of any heterogeneity by comparison of the various series.

Hardness testing was carried out on a Vickers testing machine fitted generally with a 3.162-mm. ball and employing a loading time of 1 min. to ensure that equilibrium was attained. The hardness of each specimen was determined by a series of concentric impressions made at three points on the polished surface of the specimen. The loads employed and the micrometer attachment used for measuring the impressions were both calibrated. The mean diameters for each load applied were used to calculate the value of the ultimate Meyer hardness ( $Pu$ ) by the method of averages.

The results for the series of aluminium-copper alloys were exceptional in that they showed a greater degree of scatter than the other alloys. This was thought to be due to inaccuracies in the determined values of  $n$  and was not noticeably decreased by the use of a larger indenter or higher loads. No inhomogeneities were observed in these alloys which might have accounted for the discrepancies. Suitable values were eventually obtained

by taking an average of a large number of hardness determinations.

## 2. MAGNESIUM SOLID SOLUTIONS

A much wider choice was available of elements exhibiting marked solubility in magnesium than was the case for aluminium. The solutes selected were Al (99.99%), Bi (99.9%), Cd (99.9%), In (99.96%), Pb (99.98%), Li (99.9%), Ag (99.99%), Sn (99.96%), and Zn (99.99%). The magnesium was 99.95% pure.

Materials were again melted in Salamander crucibles in a gas-fired furnace. In the absence of a flux, a coating of oxide protected the surface of the melt. Burning of the metal was minimized by careful melting and avoidance of excessive superheating. The molten alloys were poured into a preheated copper mould to give an ingot 1 in. in dia. and  $3\frac{1}{2}$  in. long. The outer surfaces of the ingots were removed by machining before homogenization by annealing for 6-9 days in the solid-solution range. The ingots were wrapped with iron wire, to prevent contact with the walls of the container, and then sealed under argon in Pyrex tubes for this heat-treatment. Subsequently the ingots were extruded to  $\frac{1}{2}$ -in.-dia. rod.

In preparing samples for hardness testing, it was found that different grain-sizes could be obtained without prior cold work by using substantially different heat-treatments before quenching to retain the solid solution. Again specimens for annealing were wrapped with iron wire and sealed under argon in Pyrex tubes.

Meyer analyses by the method of concentric impressions were used for the determination of the hardness values, although certain peculiarities of magnesium alloys necessitated modifications to the technique adopted for aluminium alloys. Difficulty was encountered with indistinctness of the perimeter of the impression due to disturbance of the boundary material. In this respect oblique illumination for measurement of impressions was found to be very useful. The trouble previously encountered with aluminium-copper alloys occurred as before. Scatter of ultimate hardness values due to inaccuracy in the determination of  $n$  was effectively reduced by using a 1-mm. ball. It was also found that a graphical determination of the ultimate Meyer hardness produced better agreement of results than calculation by the method of averages.

## 3. LATTICE-PARAMETER MEASUREMENTS

A knowledge of lattice spacings in the various alloys was essential for the investigation of relationships between hardness increment and lattice distortion. Actual determination of these values was preferred to using the results of other workers, in view of possible discrepancies in the purity of different alloys.

Powder photographs of filings taken from the surface of hardness specimens were used for these determinations. The filings were given appropriate heat-treatments, with the usual precautions to avoid contamination, and the X-ray techniques employed gave results of the usual degree of accuracy. The values obtained for the lattice parameters were in general in close agreement with those obtained by Axon and Hume-Rothery<sup>23</sup> on aluminium alloys and by Raynor<sup>24,25</sup> on magnesium

alloys. Where differences from published work were observed, these were of such a nature as to have no effect on matters discussed in the present paper.

### III.—RESULTS

#### 1. GRAIN-SIZE EFFECTS

Although it is generally acknowledged that polycrystalline metal possesses a greater resistance to deformation than single crystals, it has by no means been proved that the plastic properties of metals are sensitive to grain-size variations over the range normally encountered in industrial alloys. Thus, Karnop and Sachs<sup>26</sup> have shown that polycrystalline aluminium has a stress/strain curve very similar to that observed for some aluminium single crystals, whereas Elam<sup>27</sup> and Schmid and Boas<sup>28</sup> observed no such similarity with magnesium. Again, Barrett<sup>29</sup> has pointed out that the results of various investigations suggest that the hardness and resistance to deformation in iron increases as the grain-size is reduced, whereas Lacey and Gensamer<sup>12</sup> showed that the plastic properties of binary ferrites are rather insensitive to nominal grain-size variations, and Pfeil<sup>30</sup> indicated a similar result for hardness tests on pure iron.

Norbury<sup>2</sup> and O'Neill<sup>22</sup> consider that grain-size variations have little, if any, effect on the ultimate ball number obtained by a Meyer analysis. However, Frye and Hume-Rothery,<sup>6</sup> who also expressed hardness values in terms of the Meyer constants, suggest that their results confirm the fact that the ultimate Meyer hardness is dependent on grain-size. The examples which they give, however, show that in pure copper and pure silver the effect is only very slight over a range of grain-size between 0.1 and 2000 grains/mm.<sup>2</sup>. In recent work on the plastic properties of aluminium alloys, Dorn, Pietrokowsky, and Tietz<sup>13</sup> observed a dependence on small variations in grain-size, although they were working with materials having a grain-size large by normal standards. These and other apparently conflicting results lead to a considerable degree of uncertainty regarding the true position.

In the present investigation, the results indicate that over a considerable range the effect of grain-size on the ultimate Meyer hardness falls well within the experimental error of the hardness determinations, if indeed the effect exists at all. The following figures, which may be regarded as typical, show the results obtained with samples of magnesium-3% aluminium alloy heat-treated to give various grain-sizes:

Grain-Size in grains/mm. <sup>2</sup>	Ultimate Meyer Hardness, $P_u$ , kg./mm. <sup>2</sup>
50	81.5
112	80.2
1900	80.8

It was considered that a more accurate estimate of the hardness of an alloy would be obtained merely by taking an average of the hardness of several specimens annealed to give grain-sizes of the order of 60 grains/mm.<sup>2</sup> instead of using hypothetical formulæ for correction. This method was actually used in determining all hardness values quoted.

#### 2. ALUMINIUM SOLID SOLUTIONS

When the ultimate hardness values for the various aluminium alloys are plotted against their atomic composition (Fig. 1), a series of straight lines, all passing

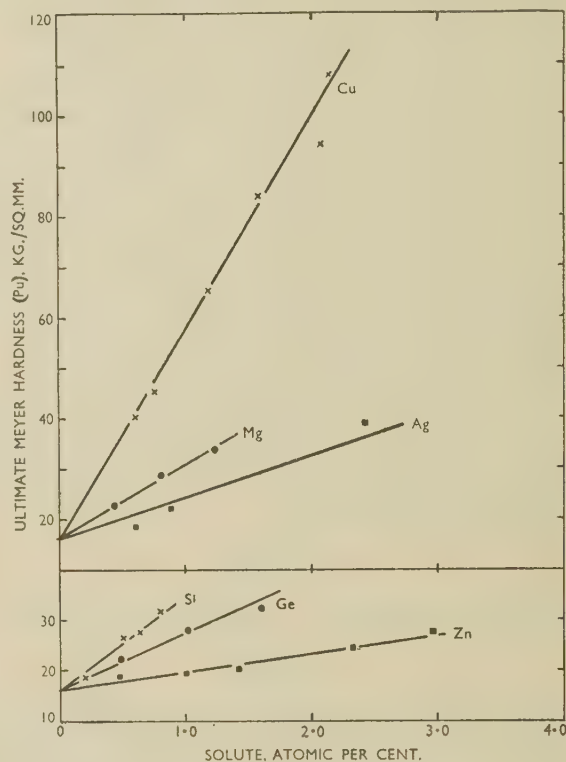


FIG. 1.—Hardness/Composition Curves for Aluminium Alloys.

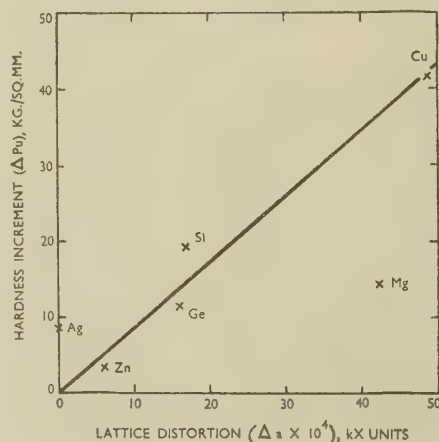


FIG. 2.—Relation Between Hardness Increment and Lattice Distortion for Aluminium Alloys.

through the point for pure aluminium, are obtained, with only a slight degree of scatter. In considering the manner in which hardness increment is influenced by variation in lattice parameter, a difficulty arises in view of the fact that there is some doubt as to the exact nature of the composition/lattice-parameter relationship. Thus, certain alloying elements have been shown<sup>13, 23, 31-33</sup> to produce a linear variation in lattice parameter only when present in excess of about 1 at.-%, smaller



quantities producing a less rapid variation. The extent of the departure from linearity is not great, however, and the values used have been obtained by assuming a linear relation over the whole range of compositions and drawing the line of closest fit to all results. If the change in lattice parameter is plotted against the hardness increment for the addition of 1 at.-% of solute, the results shown in Fig. 2 are obtained. It is seen that, with the exception of silver and magnesium, the points lie about a straight line passing through the origin. The calculation of empirical parameters, such as that used by Dorn *et al.*<sup>13</sup> in an attempt to produce a relationship with which silver and magnesium agreed, met with less success than that shown in Fig. 2.

The relative hardening effects of the elements are in the same order as that given by Dorn *et al.*, except for germanium; in this case the present work indicates less hardening than was observed by Dorn. There are two possible reasons for the difference. In the work now described more concentrated solid solutions were studied, and there is some evidence in the literature to suggest that the hardening effect of very small quantities of solute is greater than that observed in more concentrated solutions. Furthermore, Dorn *et al.* used measurements of yield strength as a means of comparing the effect of the various solutes, whereas hardness tests are now used. In so far as hardness tests may be considered to measure the yield strength of the material in the work-hardened condition—and the results of Dorn *et al.* show that germanium induces a marked increase in the strain-hardening properties of aluminium—this may offer an alternative or additional reason for the difference.

The divergences from the general rule afforded by the cases of silver and magnesium do not disappear as the result of introducing valency terms into the parameter, no matter whether the valency of aluminium is taken as 3, or, as suggested by Dorn *et al.*, as 2. It is, of course, possible to suggest that silver in aluminium is in the same category as sodium in lead and silicon in copper, the hardening being due to "chemical-affinity" effects in the absence of lattice distortion. The case of magnesium is much more difficult to explain, however, since the hardening effect is considerably less than would be expected from a consideration of the lattice distortion, as measured by change in lattice parameter.

### 3. MAGNESIUM SOLID SOLUTIONS

The relationship between ultimate Meyer hardness and the composition of magnesium alloys is slightly more complicated than that for solid solutions in aluminium. Although the points lie closely about straight lines, these do not pass through the point for pure magnesium, as shown in Fig. 3. Plots of Brinell hardness against composition considerably reduce the magnitude of the initial rapid increase in hardness with composition, and it therefore seems likely that the effect may be related to the influence of the work-hardening factor on the ultimate Meyer hardness.

With a hexagonal solvent such as magnesium, a variety of parameters might be chosen to represent lattice distortion. Fig. 4 shows that if the change in the  $a$  spacing is taken as the measure of distortion, then a quadratic relationship is observed for the hardness

increment, except with the solutes Pb, Sn, In, and Bi. The use of the volume of the unit cell as a measure of the degree of distortion yields essentially the same result. It is perhaps significant that those elements which do not appear to adhere to this relationship are the four which produce expansions in the  $c$  direction when dissolved in magnesium.

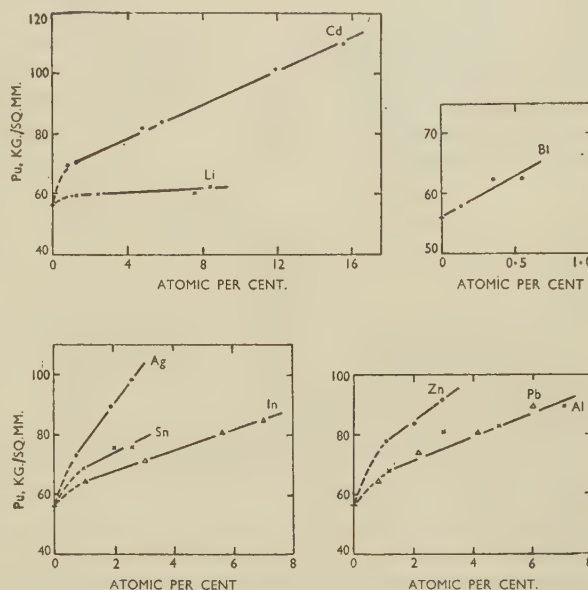


FIG. 3.—Hardness/Composition Curves for Magnesium Alloys.

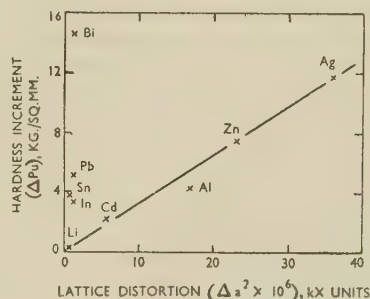


FIG. 4.—Relation Between Hardness Increment and Lattice Distortion for Magnesium Alloys.

Busk<sup>34</sup> expressed the view, confirmed by the present X-ray measurements, that the variation in the  $a$  parameter is dependent only on the atomic radius of the solute element, whereas the  $c$  parameter varies in such a way that the change in axial ratio is proportional to the variation in electron concentration. It is therefore possible to obtain a decrease in the unit cell volume accompanied by an expansion in the  $c$  direction. None of the normal parameters can therefore be expected truly to represent the extent of the distortion occurring under the combined influence of difference in atomic radius and variation in electron concentration. The fact that tin and indium do not conform to the general scheme when the  $a$  parameter is used as the measurement of distortion, indicates that the valency factor is more prominent here. The same applies to lead and bismuth, though in these cases there is the additional

influence of a solute atom larger than that of the solvent. With bismuth the hardening effect may also be accentuated by the fact that, as compared with the other alloys, those containing bismuth were very dilute, and there are indications that the hardening effect is less strong for more concentrated solutions.

If the hardness increase is plotted against the axial ratio for solutions of Cd, In, and Sn, the results fall on a straight line; since these elements belong to the same row of the Periodic Table this again suggests an electron-concentration effect. The case of silver, which also belongs to this row of the Table, may indicate that a decrease in electron concentration is more effective in promoting hardening than an increase.

#### IV.—DISCUSSION

The results conform to the general pattern of those already to be found in the literature, in that they indicate that the hardening effect of solutes, with certain exceptions, is related to the distortion produced in the solvent lattice. The theories developed by Mott and Nabarro may therefore be expected to account for the results in a general fashion, since they are based upon a model in which the resistance to motion of dislocations is caused by distortion of the lattice. However, in considering the application of these theories in detail to the present results, a difficulty arises because, although lattice distortion appears to be the governing factor in the case of both aluminium and magnesium solid solutions, the hardness of the former is linearly dependent upon distortion, whereas the latter show a quadratic relationship. In an early paper, Nabarro<sup>17</sup> suggested that these were in fact limiting conditions of the same relationship, a linear relationship being observed when the hardness increment was large compared with the hardness of the solvent metal, and a quadratic relationship when the hardness increase was small in relation to the hardness of the pure metal.

This is certainly the case for the results of the present work, aluminium being hardened to a much greater extent than magnesium by elements in solid solution. However, the theory also requires that concentration should exercise a similar influence, and this is not borne out by the results now obtained. In actual fact the power of various solutes to harden magnesium appears to decrease in more concentrated solutions. Moreover, the suggestion would require that the type of relationship should not be dependent on the solvent alone and that those solutes which have little hardening effect should exhibit a quadratic dependence of hardness on distortion, whilst those which produce marked hardening should yield a linear relationship. Results reported so far do not exhibit a sufficiently close relationship to allow differentiation to be made between a continuous quadratic relationship and one which in fact becomes linear when hardening is more marked.

It would appear, therefore, that the varying dependence of hardness on lattice distortion has some real significance beyond that suggested by Nabarro. In their later papers, Mott and Nabarro<sup>18,35</sup> introduced the idea of the flexibility of dislocations and obtained different powers for the lattice-strain component according to the

assumption made as to the length of dislocation which moved as a coherent piece. Mott<sup>35</sup> suggested that the decision as to the effective power of the strain component was not possible on the basis of the experimental evidence available. This may well be the case, but it also seems reasonable to suggest that the effect of lattice strain may not be the same for all solvent metals. Despite the slight discrepancies in detailed application, the original Nabarro equation gives a close approximation for the general behaviour of solid solutions and may be employed empirically to estimate hardening effects.

As with those published results dealing with other solvent metals, the present results indicate that hardening may occur by the operation of factors other than that of lattice distortion, as measured by change in lattice parameter. Thus silver hardens aluminium without attendant lattice distortion and Pb, Sn, In, and Bi produce more hardening in magnesium than would be expected from a consideration of the parameter which measures the hardening effect of other solutes.

It has been usual in the past to ascribe such exceptions to the general hardness/lattice-distortion relationship to chemical or valency effects, i.e. where the hardness was greater than would be expected from a consideration of the effect of the solute upon the lattice parameter, it was assumed that some form of chemical bonding strengthened the metal. It is difficult, however, to understand why chemical strengthening should operate only in those cases where the hardening cannot be simply explained in terms of lattice distortion, and a much more logical approach would appear to be that adopted by Dorn *et al.*,<sup>13</sup> who explain the hardening in terms of a composite function of valency and lattice distortion. The experimental evidence certainly indicates that solid-solution hardening may be related to valency effects, but the incorporation of these into empirical equations is not entirely satisfactory. Thus, lattice strain, as measured by change in lattice parameter, is itself dependent upon the relative valencies of solvent and solute,<sup>36</sup> and it may therefore be argued that chemical and electronic effects are already allowed for in the manner in which distortion is measured. Herein may lie the real problem. Whereas lattice-parameter measurements yield a quantity which is an averaged measure of lattice strain, what is probably required is an indication of the local strain in the lattice surrounding solute atoms. Nor should the contribution which clustering may make to hardness be ignored, since it could explain the otherwise unaccountable hardening occurring in alloys such as those of the aluminium-silver system.

It may well be that the difficulties associated with a complete explanation of the mechanism of solid-solution hardening will not be surmounted until these and other aspects of the methods employed in studying the subject experimentally have been given more attention. Thus, in the work so far carried out, a variety of ways have been adopted of assessing the hardening in alloys of varying grain-size and degrees of purity.

In considering these results as a whole, however, it would appear that the Mott and Nabarro theory based on lattice strain is likely to prove of greatest value to the metallurgist interested in the development of new alloys. Nabarro<sup>17</sup> has tested the theory by calculating the value of the dimensionless constant  $\alpha$ , by which he relates lattice strain to hardening, using the results of Frye and



Hume-Rothery.<sup>6</sup> His calculations give a value for  $\alpha$  which approximates closely to the predicted value of 0.05. When the present results are similarly treated, they yield values of 0.06 and 0.055 for aluminium and magnesium alloys, respectively, thus confirming that the equation may be successfully used to give an approximate estimate of solid-solution hardening. Certainly, if lattice strain were used as an indicator of the hardening to be expected on alloying, the results of the present and previous work show that, almost invariably, the most useful hardening elements would have been correctly chosen. In those cases where the degree of hardening is not in reasonable agreement with the predictions from the Mott and Nabarro theory, the discrepancy is rarely so great as to be of importance from the point of view of alloy development.

### V.—CONCLUSION

It is suggested that the hardening of metals by elements in solid solution is primarily dependent upon the extent to which the lattice is distorted by the presence of the solute atoms and that it can be generally estimated by application of the Nabarro equation. In a few cases the hardening is greater than would be expected from a knowledge of the lattice distortion. A full explanation of these observations is dependent upon a more complete understanding of the reasons for lattice-parameter changes on alloying, but in magnesium alloys it appears that the distortion, and therefore the hardening, is basically related to the difference in atomic diameters of solvent and solute, with the exceptions to the general rule showing additional hardening attributable to electron-concentration effects.

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# The Constitution of Copper-Rich Alloys of the Copper-Manganese-Aluminium System

By D. R. F. WEST and D. LLOYD THOMAS

(*Journal*, this vol., p. 97)

Dr. R. HAYNES,\* B.Met., A.I.M. (Member): It is interesting that the authors have obtained direct experimental evidence of the ordering of the  $\beta$  phase and have been able to relate this to the metastable ( $\beta + \beta_1$ ) structures observed in the binary copper-aluminium alloys. Indirect evidence † had previously pointed to the occurrence of ordering of the  $\beta$  phase below the eutectoid temperature, and it had been associated with the  $\beta \rightarrow \beta_1$  transformation. These inferences are supported now by more direct evidence.

The marked inflection in the curve  $FE$  in Fig. 10, which is associated with ordering in the  $\beta$  phase, is noteworthy, since, from qualitative thermodynamic considerations, a rapid change in the composition of the parent phase in equilibrium with  $\alpha$  and  $\gamma$  is to be expected within a narrow range of alloy composition if the range of stability of the new phase is appreciably less than that of the old, as appears to be the case.‡

An eutectoid composition of 12.5% aluminium is quoted by the authors for the  $\beta_1 \rightarrow (\alpha + \gamma_2)$  transformation in the binary system, but the eutectoid temperature is not stated. Earlier, it had been predicted that the eutectoid temperature † § should be higher for  $\beta_1$  than for  $\beta$ , and that the eutectoid composition † should be richer in aluminium for  $\beta_1$  than for  $\beta$ . Clearly, it is impossible to determine the eutectoid temperature as defined above, but it has been shown that, in copper-aluminium alloys close to the eutectoid composition, the composition of  $\beta$  or  $\beta_1$  that transforms to eutectoid changes progressively with decrease in transformation temperature down to about 100° C. below the eutectoid tempera-

ture,† the composition of the  $\beta$  or  $\beta_1$  being the composition of  $\beta$  or  $\beta_1$  in metastable equilibrium with  $\alpha$  or  $\gamma_2$  at the transformation temperature. If the true eutectoid temperature cannot be determined, as in this case, it would be informative if the temperature to which the "eutectoid composition" relates and the phase ( $\alpha$  or  $\gamma_2$ ) with which  $\beta$  or  $\beta_1$  was in equilibrium before the eutectoid transformation, were stated.

THE AUTHORS (in reply): Dr. Haynes has referred to the temperature and composition of the  $\beta_1 \rightarrow (\alpha + \gamma_2)$  eutectoid in binary copper-aluminium alloys. We have no evidence for doubting the prediction that the temperature of this transformation is above 565° C. The interlamellar spacing of the eutectoid formed from  $\beta_1$  during isothermal transformation at 400° C. is not appreciably less than that formed at 500° C., an observation that suggests that the eutectoid temperature is well above 500° C.|| The eutectoid composition is very near to 12.4% aluminium. This value has been deduced from the results of isothermal transformation of two binary alloys, containing 12.35 and 12.5% aluminium, respectively.|| Transformation, either at 500° or at 400° C., produces mainly pro-eutectoid  $\alpha$  in the alloy containing 12.35% aluminium and pro-eutectoid  $\gamma_2$  in the alloy containing 12.5% aluminium. These and other results || have led to the conclusion that the composition of  $\beta_1$  that transforms to lamellar eutectoid is virtually independent of transformation temperature. It is hoped that the results referred to above will be published in greater detail at some future date.

\* Technical Officer, Imperial Chemical Industries, Ltd., Metals Division, Birmingham.

† R. Haynes, *J. Inst. Metals*, 1954-55, **83**, 105.

‡ D. Lloyd Thomas, *ibid.*, p. 559 (discussion).

§ C. S. Smith and W. E. Lindlie, *Trans. Amer. Inst. Min. Met. Eng.*, 1933, **104**, 69.

|| D. Lloyd Thomas, unpublished work.



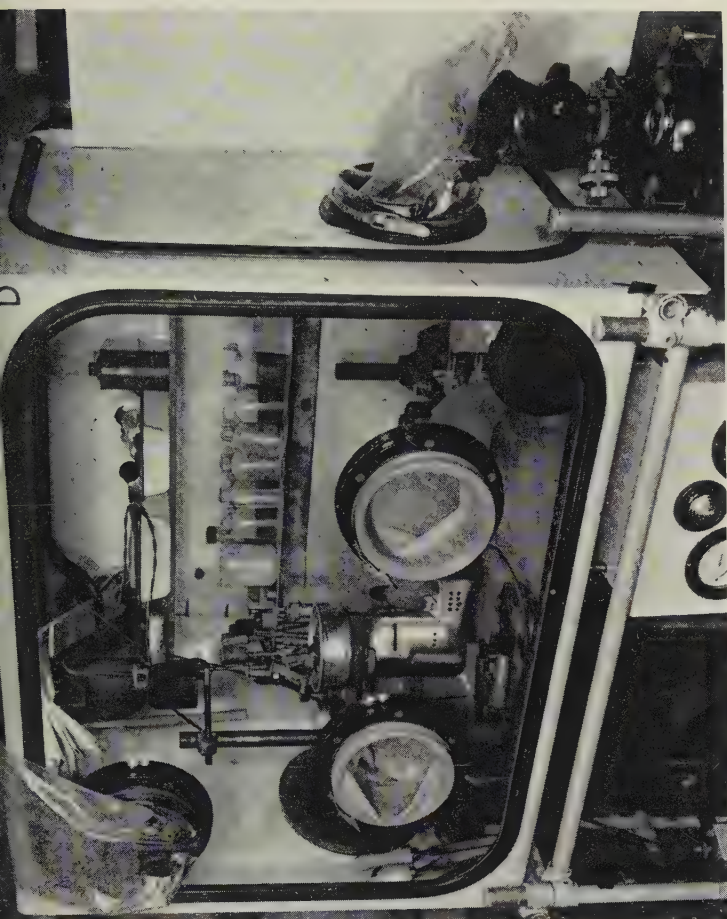


FIG. 7.—The Metallography Box. Mechanical polishing is done on the small lap driven by the inverted electric drill. The speed is controlled by a knee-operated Variac below the box. A windscreen-wiper motor mounted above the drill reciprocates the specimen during automatic polishing. This is the standard glove-box shell  $39 \times 24 \times 29$  in. high. The flange at the near end is used to bolt the box on to a panel on the active workshop area if modifications are required.

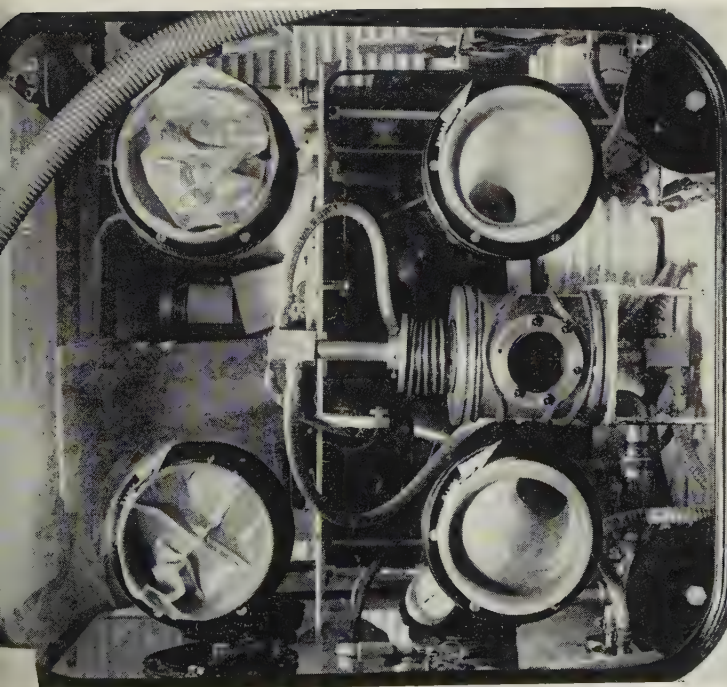


FIG. 6.—Close-Up of the Alloy-Preparation Box. The arc-furnace is in position. The resistance furnace is at the back. The balance, on the shelf, is worked from the two glove-ports on the left-hand face. The balance-case is tilted for convenience in working, although the balance is vertical. Vacuum pumps are housed in a separate, lower box. Bung, in the front corners of the box, are pulled into the glove-ports and the gloves withdrawn when the box is not in use.

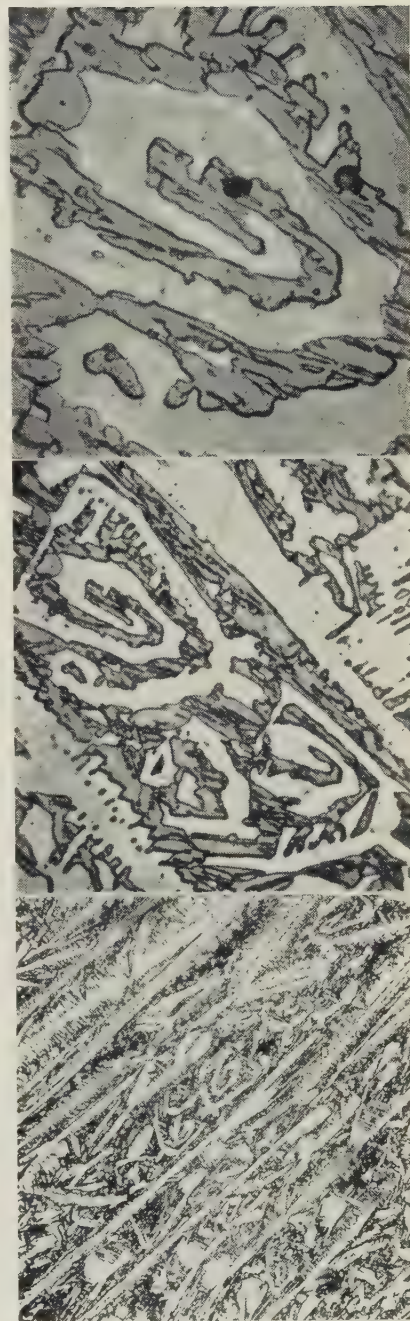


FIG. 8.—Photomicrographs of a Plutonium-75 at.-% Gold Alloy as Viewed Through a Clear Plastic Bag. Diamond polish. Electro-etched in 30% HCl in alcohol at 20 V. (a)  $\times 90$ , (b)  $\times 360$ , (c)  $\times 900$ , oil immersion.



## MICROSTRUCTURES OF COMPRESSED 70:30 BRASS.

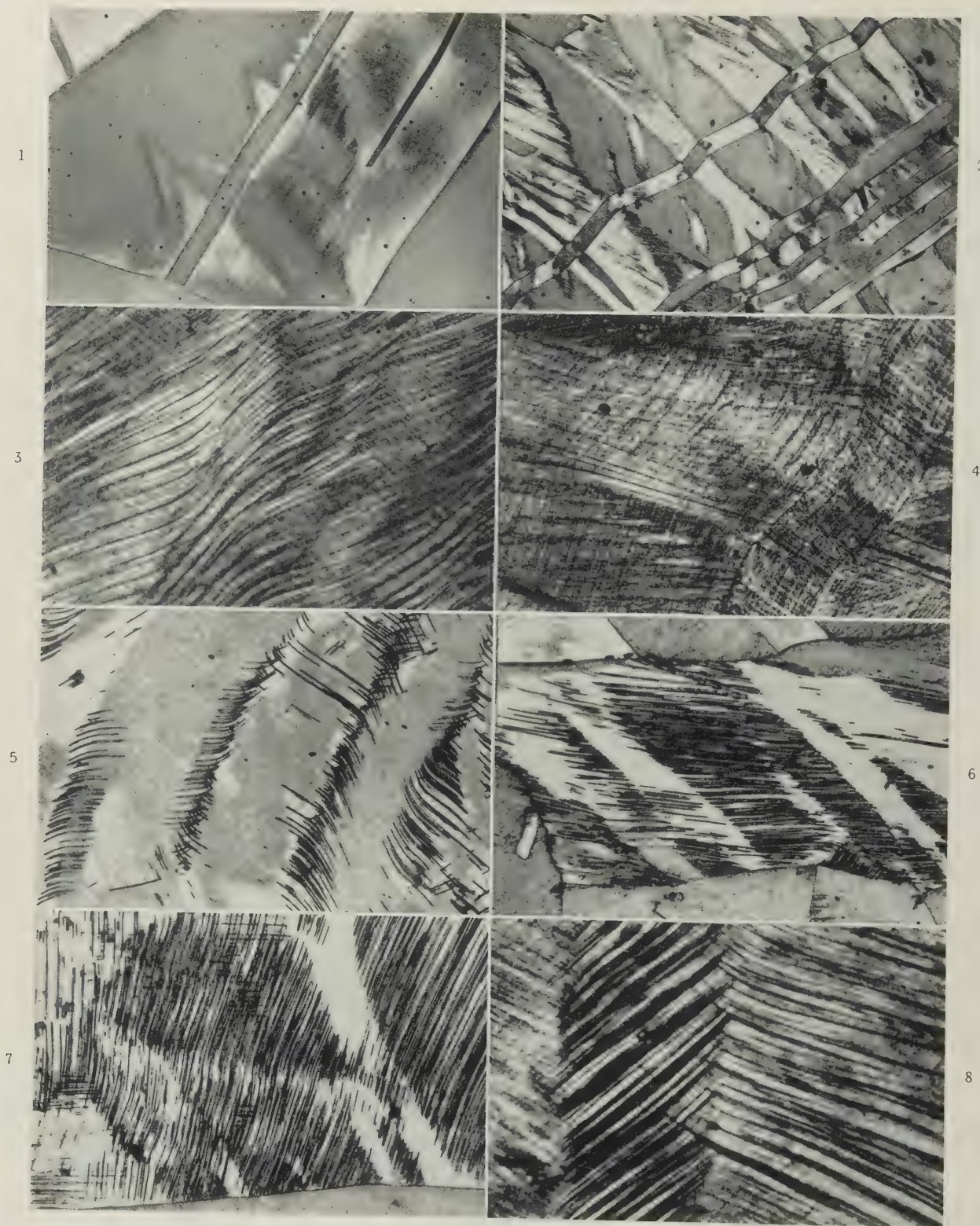


FIG. 1.—4.6% Compression at 300° C. Etched in ferric chloride reagent.  $\times 500$ .  
 FIG. 2.—11.8% Compression at 20° C. Etched in ferric chloride reagent.  $\times 100$ .  
 FIG. 3.—19.8% Compression at 20° C. Electrolytic thiosulphate etch.  $\times 500$ .  
 FIG. 4.—Portion of field of Fig. 2. Electrolytic thiosulphate etch.  $\times 500$ .  
 FIG. 5.—27.7% Compression at 300° C. Etched in ferric chloride reagent.  $\times 500$ .  
 FIG. 6.—44.5% Compression at 300° C. Etched in ferric chloride reagent.  $\times 500$ .  
 FIG. 7.—19.8% Compression at 20° C. Etched in ferric chloride reagent.  $\times 500$ .  
 FIG. 8.—19.8% Compression at 20° C. Electrolytic thiosulphate etch.  $\times 1000$ .



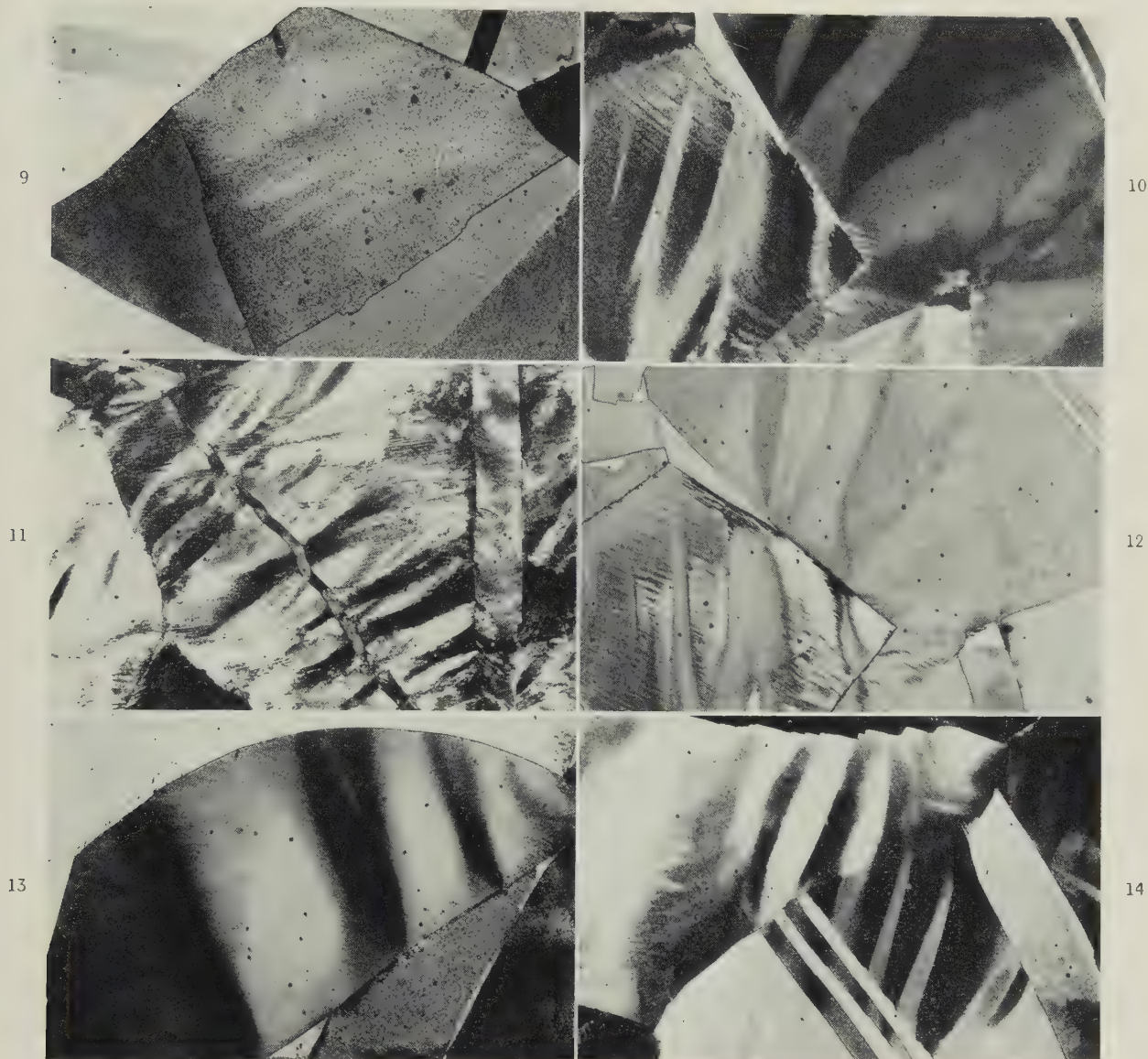
MICROSTRUCTURES OF COMPRESSED 70 : 30 BRASS.  $\times 100$ .

FIG. 9.—2.2% Compression at 20° C. Etched in ferric chloride reagent. Polarized light.  
 FIG. 10.—11.8% Compression at 20° C. Etched in ferric chloride reagent. Polarized light.  
 FIG. 11.—19.8% Compression at 20° C. Etched in ferric chloride reagent. Polarized light.  
 FIG. 12.—As for Fig. 10. Bright-field illumination.  
 FIG. 13.—12.3% Compression at -183° C. Etched in ferric chloride reagent. Polarized light.  
 FIG. 14.—12.8% Compression at 300° C. Etched in ferric chloride reagent. Polarized light.

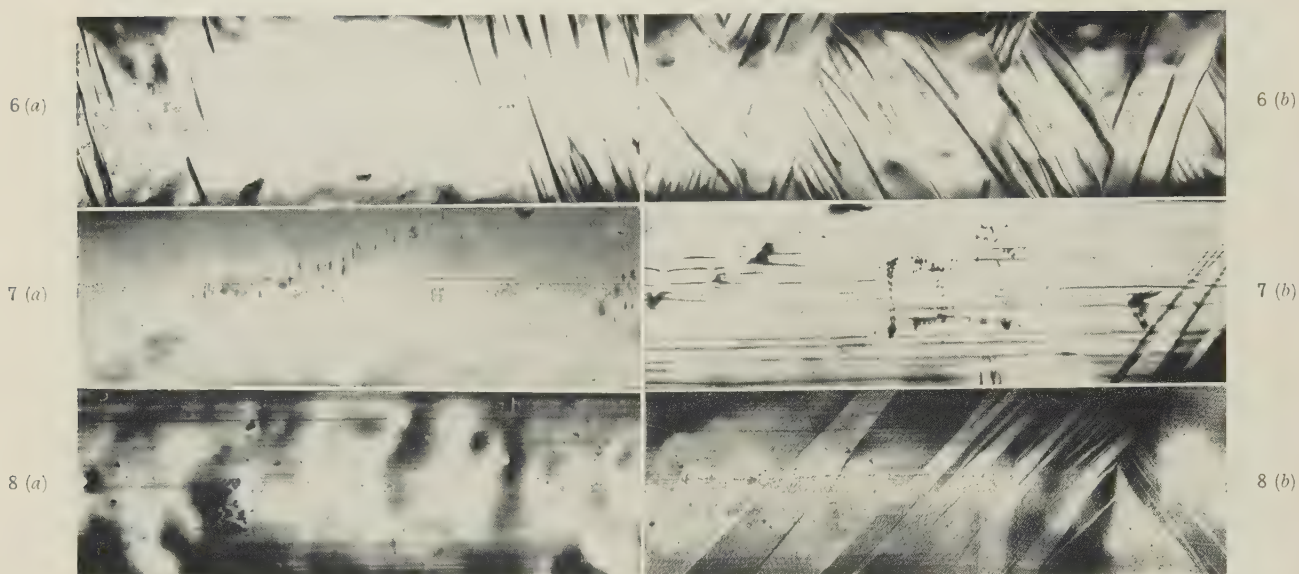
PHOTOMICROGRAPHS OF ZINC SINGLE CRYSTALS.  $\times 75$ .

FIG. 6.—Twin Distribution in the Longitudinal Direction of (a) Clean and (b) Copper-Coated Crystal. Etched.

FIG. 7.—Basal Slip Lines on the Longitudinal Surface of a Clean Crystal Strained (a) 0.0% and (b) 2.5%. Unetched.

FIG. 8.—Basal Slip Lines on the Longitudinal Surface of a Copper-Coated Crystal Strained (a) 0.0% and (b) 2.5%. Unetched.



## SOME ASPECTS OF PROGRESS IN THE NICKEL INDUSTRY \*

By L. B. PFEIL,† O.B.E., D.Sc., F.R.S.

### SYNOPSIS

An account is given of some of the important advances that have been made in recent years in prospecting for nickel ores, ore concentration, and the smelting and refining of nickel. In conclusion, some present-day applications of the metal and its alloys are described.

### I.—INTRODUCTION

ALTHOUGH it is the privilege of the newly-elected President to choose for his address any subject that falls within the wide interests of the Institute, I must confess I found difficulty in deciding what I could speak about this morning which would be of some interest to my fellow-members and our guests.

I was forced to the conclusion that the subject must be something to do with the nickel industry, since this has been my essential interest for the past 25 years, and the problem thus became one of avoiding an ill-timed technical lecture and of devising a Presidential Address which would not fall too far behind the standard set by previous Presidents.

My plan now is to outline some of the stages in the progress of the nickel industry which I myself have found of special interest, and which I hope may be of some interest to you also. I am going to offer no balanced survey of the industry—I am, indeed, going to pass over several major developments, either because of the time factor or because I have no first-hand knowledge of the subject.

### II.—PROSPECTING

It is, of course, well known that Canada is the principal source of the metal nickel, with the major developed ore deposits lying in the Sudbury area of Ontario. Here the nickel occurs as sulphide, as also does copper, each to the extent of roughly 1% in the ore mined. Essentially, the treatment of the ore consists of crushing and grinding, differential froth-flotation of the sulphide, smelting the nickel-rich concentrate to give a nickel-sulphide matte containing some copper sulphide, separating the nickel sulphide from the copper sulphide, converting the nickel sulphide to oxide, and finally refining to give electrolytic nickel or Mond pellet nickel.

Nickel sulphide (pentlandite) commonly occurs in association with much larger proportions of iron sulphide (pyrrhotite). Pyrrhotite is magnetic, and this property has played a significant part in recent years in facilitat-

ing the search for new ore bodies. Members will be well-familiar with the effect of a magnet on the compass needle. Equally, a large mass of magnetic iron sulphide, even at a considerable depth in the earth's crust, can influence the instrument known as the magnetometer.

In so vast a country as Canada prospecting by teams of men on the ground is slow and costly in labour. The introduction and development of airborne geophysical exploration by magnetometer inspection, followed by the use of airborne electromagnetic gear which records data on the electrical conductivity of rock formations, are of particular interest, in that these procedures have brought about a major change in the speed and cost of prospecting. An aircraft carrying recording geophysical instruments, together with a synchronized cine-camera, is flown at a low height across the territory, along paths about half a mile apart. In some circumstances, for example when flying over water, radar may be used so that the location of magnetic and other anomalies can be accurately plotted. The records obtained are studied and areas of possible interest are delineated on the map. Subsequently, prospecting teams on the ground investigate the selected areas by diamond drilling and the like.

To provide some quantitative indication of the importance of airborne prospecting, figures may be quoted for the work carried out by The International Nickel Company of Canada. It has been reported that, in a single year, 24,000 miles were flown and during the past 10 years nearly £1,000,000 were expended by the Company on airborne exploration. This, of course, is only a part of the story, for in this same period the Company spent a total of more than £10,000,000 on exploration for new nickel deposits.

The detection of anomalies is a far cry from finding nickel ore or, indeed, from demonstrating that anything of value is in the offing. Experience proves, however, that exploration for nickel in the region of certain types of anomaly is much more likely to be successful than elsewhere.

A year or two ago it was announced that a zinc-silver-copper mine was under development in the

\* Delivered at the Annual General Meeting, London, 30 April 1957.

† Director, The Mond Nickel Co., Ltd., London.

Bathurst-Newcastle area of New Brunswick, and that a 25% interest in the mine had been received by The International Nickel Company of Canada in return for the geophysical work that had initiated the mine development. Less than a year ago, ore reserves in this mine were reported to be 7,000,000 tons, with a combined lead-zinc-copper content of 10% and a valuable silver content.

A more recent and more spectacular success, following airborne geophysical prospecting and other forms of exploration, is an 80-mile by 5-mile-wide mineralized area located in Northern Manitoba, some 400 miles north of Winnipeg and centred in an area of some 150,000 square miles almost devoid of industry. Bearing in mind that access to this area—Mystery and Moak Lakes—has been possible in summer only by air, and that heavy equipment can at present be transported only in winter over the snow, the contribution of airborne exploration can be appreciated. Some £4,000,000 has been expended in exploring the Mystery/Moak area, but by the time nickel is commercially available from the mine, in 1960, the outlay will have exceeded £50,000,000.

### III.—ORE CONCENTRATION

The major nickel deposits currently being mined in the Sudbury area are substantially lower in grade than the ore mined before the war. It will, therefore, be appreciated that the costs of mining must be kept low. This is scarcely the occasion to describe the research and development work that has been successfully applied by Inco to this end. Suffice it to say that economies in mining practice, such as the panel-caving which provides 10,000 tons of ore per day from the Creighton mine, have played an important part in the prosperity of the nickel industry.

In concentrating these low-grade nickel ores, froth-flotation plays a vital role. For more than 50 years it has been known that when finely-ground ore is suspended in aerated water some minerals are readily wetted and sink, while others, being air-avid, will adhere to air bubbles and be carried to the surface. In recent years much research has been carried out bearing on this phenomenon; for example, studies of "promoters", which alter the wettability of the mineral particles (I avoid the terrible word "hydrophobicity"). Again, research has been active on frothing agents, which help the formation of stable air bubbles of the desired size, whilst numerous other variables, such as acidity, temperature, particle size, and surface texture of the minerals, have also received attention.

Such research and development has made it practicable and economical to separate the finely-ground Sudbury ore into four fractions: (a) a nickel-sulphide-rich concentrate, (b) a copper-sulphide-rich concentrate, (c) an iron-sulphide-rich concentrate, and (d) waste rock, of no value.

Discarding the rock waste at an early stage and sending the bulk of the iron to a separate circuit not only greatly reduce the weight of material to be smelted, with a saving in cost and increase in useful smelter capacity, but have led also to the marketing of a premium grade of iron ore made from the iron sulphide, which iron was formerly converted into slag and dumped.

### IV.—EXTRACTION

It is not practicable, by the differential froth-flotation of Sudbury nickel-copper ores, to obtain nickel sulphide completely free from copper, and the more complete separation of these two metals is an essential further step. The classical treatment for the separation of nickel sulphide from copper sulphide is that known as the Orford process, in which the first step is smelting to produce a molten nickel-copper-sodium sulphide matte. Such a matte separates, on cooling, into two layers—the upper layer consisting of copper-sodium sulphide and the bottom layer of nickel sulphide. To obtain nickel substantially free from copper, the separation process has to be repeated, thus rendering the treatment complicated and expensive.

In the Copper Cliff smelter of The International Nickel Company, the Orford process has been replaced by the so-called controlled-cooling process, which is a major improvement in smelter practice. The fundamental background of the process is provided by the nickel-copper-sulphur ternary equilibrium diagram, which demonstrates that, on slow cooling of a nickel-copper matte, three separate phases can be obtained.

In the compositions of present interest, the first solid to separate from the molten material is copper sulphide,  $\text{Cu}_2\text{S}$ , then actual metal crystallizes in the form of an alloy containing about 80% nickel and 20% copper, and finally a nickel sulphide,  $\text{Ni}_3\text{S}_2$ , containing some copper in solution, solidifies. On further cooling, the  $\alpha$ - $\text{Ni}_3\text{S}_2$  changes to the  $\beta$  form, with the rejection of dissolved copper.

Given very slow cooling, the primary copper sulphide forms in large crystallites; the metallic particles are coarse, and the copper rejected by the transformed nickel sulphide joins the primary copper-sulphide crystallites.

Such a slowly solidified mass may be comminuted, and the metallic fraction can be extracted by a magnetic separator. As a bonus, precious metals, platinum, gold, &c., join the metallic portion, which may be less than 20% of the whole, and are thus readily amenable to early recovery.

By employing froth-flotation, the nickel and copper sulphides can readily be separated with a mutual contamination not exceeding 1%, and its introduction, and the elimination of the Orford separation, can fairly be described as a milestone in the progress of the nickel industry.

### V.—REFINING

The refining of nickel in the Sudbury ores cannot be dissociated from the refining of copper, since these two metals occur in about equal quantities. An interesting innovation in recent years has been the oxygen flash-smelting of the copper-sulphide concentrate. The sulphide is treated as if it were pulverized coal and is blown into the furnace with oxygen. The burning of the iron sulphide in the concentrate provides sufficient heat to give a molten copper-sulphide matte and an iron-rich slag. Apart from saving fuel, this process yields a gas so rich that liquid sulphur dioxide can readily be condensed out, and this product is of great value in the important Canadian paper-pulp industry.

The magnitude of this flash-smelting operation may



be judged from the fact that more than 100,000 tons of oxygen and 70,000 tons of liquid sulphur dioxide are produced annually, with a saving of 60,000 tons of coal.

The most recent change in Copper Cliff refining practice has been the setting up of a separate circuit for the iron-rich flotation concentrate. The treatment is designed not only to produce a high-grade iron ore for steelmakers, but also to recover the nickel values in the iron sulphide. The iron sulphide is fluid-bed roasted to oxide; air is blown up through a bed of the hot sulphide, so that no mechanical stirring or raking devices are required. The finely-divided oxidized material is carried away by the gas stream, collected in a cyclone, and then fed into a reduction kiln, where conditions are so adjusted that nickel, but only a little iron, is reduced. Then follows an atmospheric ammonia-leaching treatment whereby the nickel is dissolved, to be recovered later as nickel carbonate. Finally, the iron oxide is pelletized, to give walnut-sized material particularly suitable for adding to steel furnaces.

This passing reference to the recovery of iron ore, and of nickel by leaching, is only one example of the current importance of hydrometallurgy in nickel extraction. Other outstanding examples of such processes are those employed by the nickel companies in Cuba and by Sherritt Gordon in Manitoba.

Whereas a considerable amount of nickel is marketed as oxide—a form which can readily be used by steelmakers—the bulk of the production is further refined, either electrolytically or by the Mond carbonyl process.

Electrolytic treatment has been considerably improved in recent years by the replacement of the older sulphate electrolyte by a sulphate-chloride solution, and by the use of addition agents which prevent the formation of honeycombed deposits.

While the new type of electrolyte is more corrosive, the electric-power requirements are reduced, a higher anode current efficiency is obtained, and the recovery of cobalt is facilitated.

When originally established, over 50 years ago, the Mond process was designed to treat a nickel-copper matte. The essential stages were:

- (a) Roasting to eliminate sulphur.
- (b) Leaching with sulphuric acid, to remove copper as copper sulphate.
- (c) Reduction of the residual nickel oxide to finely divided metal, by means of the hydrogen in water gas.
- (d) Volatilization of the nickel as carbonyl gas, by reaction with the carbon monoxide in water gas.
- (e) The decomposition of the nickel carbonyl on the surface of nickel particles, resulting in gradual growth into the familiar Mond pellets.

Today the operations are significantly different. Firstly, the bulk of the copper is extracted by the procedures which have already been outlined: secondly, the sulphur is largely eliminated in Canada, in a sintering machine. As a result of these changes, stages (a) and (b) have disappeared from the flow-sheet of the Mond plant at Clydach, South Wales.

A most important contribution to economical operations at Clydach has been made by fundamental and process research, which has been concerned with gas-metal reactions and velocities. Without going into

technical details, some idea of the progress that has been made is presented by the fact that, of the seven plant units at Clydach, four are now out of service. The remaining three units have today a production capacity such that more pure nickel was produced in the form of pellets at Clydach in 1956 than ever before in the history of The Mond Nickel Company.

Notwithstanding this, it is only fair to the pioneers of the carbonyl process to say that the design and layout of the reducer, volatilizer, and decomposer units in operation have remained for over 50 years essentially the same. Only during the past year have plans been developed for the reconstruction of the Clydach plant, taking advantage of the information that has been gathered by many years of research.

## VI.—USES OF NICKEL

I propose to conclude this address by a few remarks regarding the applications of nickel in industry.

I think that few of you will quickly be able to think of an application where nickel can be seen in service, and perhaps I may say, without being accused of advertising, that nickel has been described in the course of sales development as "Your Unseen Friend". There are some, but relatively few, exceptions to this "unseen". There are pure nickel coins in circulation, though not in this country, and there is a widespread use of nickel for saucepans and the like, but in hotels rather than in private houses. Nickel parts can be found in radio valves, nickel equipment is used in some types of chemical processing plant, and a peculiarly interesting use of nickel which has more recently been developed is its application in echo depth-sounding equipment, where the unusual magnetostrictive properties of the metal are utilized.

Nickel is, however, essentially an alloying element, the introduction of which into other metals leads to the development of alloys possessing special properties. Outstanding examples are the austenitic stainless steels, generally containing 8% nickel and 18% chromium. Because of their special properties, the demand for these steels has been steadily increasing over the past few years, and at the present time about one-third of all the nickel available in the free world is so used, representing the largest consumption of the metal in any single field of application.

The chemical industry, which demands highly corrosion-resistant materials, has for a long time made extensive use of stainless steels, and in recent years such materials have played a prominent part in atomic-energy developments. The food industry and the domestic field are making increasing use of stainless steel and, looking to the future, it seems likely that important advances will be made in their adoption for architectural purposes.

Second only to stainless steel is the use of nickel in constructional alloy steels, an application which until recently was the biggest single consumer. It was recognition of the fact that the addition of nickel to steel gives a stronger and tougher product which, some sixty years ago, stimulated increased nickel production and, over the years, has been largely responsible for the development of the industry. It is interesting to note



that the favourable influence of nickel in alloy steel, now couched in terms of hardenability, depth-hardening, and transformation characteristics, was recognized by much more "rule-of-thumb" methods so long ago.

The situation which has now existed for some years, whereby the demand for nickel has exceeded the supply, has naturally led to the exercising of the greatest possible economy in its use. As a result of extensive research work on alloy steels, both here and abroad, we now know much more about the fundamental effects of nickel, both alone and in combination with other alloying elements such as chromium and molybdenum. So much so that double- and triple-alloy steels containing lower amounts of nickel have largely superseded the straight nickel steels previously used.

It would, however, be incorrect to generalize too widely on this tendency towards reduced nickel contents; where particularly onerous service conditions obtain, such as, for instance, in the case of heavy-duty gears, preference is still given to the higher-nickel steels, containing up to 4½% nickel.

A further field which has undergone some interesting changes during my years in the nickel industry is that of plating. The amount of nickel now used as an electro-deposited underlay to chromium is estimated as some 15% of the nickel available in the free world.

Since the chromium coating is so thin, 10–20 millionths of an inch, it provides little more than a tarnish-resisting bright surface. The function of the nickel undercoating is to protect from corrosion the baser constructional metals which give the parts the required strength and rigidity. During recent years the study of nickel plating on a more fundamental and scientific basis has resulted in a better appreciation of the characteristics required of the electrodeposited metal, and of how to control production operations so as to obtain the best results. Unfortunately, the shortage of nickel in recent years has rendered it impossible for electrodepositors to adopt the specifications recommended for nickel plating and, hence, we have seen abnormally early deterioration of chromium-plated parts exposed to the vagaries of the British climate.

Perhaps the use of nickel in which I have personally been most interested is that in gas turbines, where components have to function under high stresses at temperatures above a red heat. My particular interest here stems from researches I undertook between 1920 and 1930 on the fundamentals of scaling at high temperatures.

After 1930 I became increasingly involved in the study of nickel-chromium alloys, with special reference to the wire which is used in electrical-heating appliances. In the 1930s we were rather surprised when researches showed that elements present in no more than traces could play a vital part in determining the heat-resisting qualities of an alloy. Less than 1 part in 1000 of cerium (a component of the lighter flint) was found to increase the test life of 80:20 nickel-chromium wire for domestic electric heaters by a factor of ten. How often does anyone experience a failure of an electric fire today—except by knocking it over, and the like?

The realization of the significance of minor elements in modifying the properties of the nickel-chromium alloys of this type was, however, destined to prove much more widely applicable, and the successful development of the aircraft jet engine was closely associated with the

development of alloys based on the 80:20 nickel-chromium alloy for electric fires. Obviously this material would not burn away or oxidize appreciably at high temperatures, but it was not strong enough to resist the high stresses to which jet-engine components were subject, and some means had to be found to make the alloy stiffer at high temperatures without rendering impossible the fabrication of complex components by forging, rolling, &c.

The solution was found by the introduction of additional elements that rendered the alloy precipitation-hardenable. At the forging temperature, the modified alloy is single-phase and soft; at the somewhat lower temperature involved in jet-engine service, precipitation of a second phase occurs, giving the desired stiffening effect. Thus came into existence the Nimonic series of alloys—electrical-resistance-wire material stiffened by the introduction of titanium and aluminium.

There have, of course, been subsequent developments. The designers of jet engines and gas turbines continually demand improved alloys for operation at higher temperatures, and research on high-temperature materials has been active all over the world. The merits of further additions, such as cobalt and molybdenum, have been ascertained, and commercial developments have followed.

Great interest and considerable technical importance lie in research results which have been obtained in this field regarding the influence of trace impurities. Advances which have been made in the purity of raw materials, the development of spectrographic techniques and the introduction of the mass-spectrograph for the analysis of alloys, and improvements in vacuum melting and casting have made researches on trace elements practical and effective.

In heat-resisting alloys there are two sorts of trace elements—the good and the bad. Amongst the good, reference has already been made to cerium; one could add zirconium, calcium, thorium, and boron. On the bad side, lead, tin, and bismuth might be scheduled, together with sulphur and selenium. Maybe research will show in the future that there is a third type of trace element—the inert type—but it is abundantly clear that trace elements in general play a vital part in the quality of many metallurgical products. Control over these effects falls into the field of "know-how" and can scarcely be taken into account in specifications.

A recent and particularly interesting example of the outstanding effects of small additions is to be seen in the influence of small amounts of magnesium or cerium in cast iron. This brittle metal, with its strength sapped by graphite flakes, is, by the introduction of less than 1 part in 1000 of magnesium or cerium, converted into a ductile iron that can be bent and shaped almost like steel. In these treated irons the graphite forms innocuous spheroids, and the characteristic brittleness of cast iron disappears, to the great advantage of the engineer.

I have spoken of stainless steels, alloy steels, high-temperature alloys, and plating; these, together, take up two-thirds of the free world's nickel supplies. The balance of the nickel goes into a multitude of applications, of which, tonnage-wise, nickel-copper alloys are of the greatest importance. They range from Monel, which is two-thirds nickel and one-third copper, down to



cupro-nickel, in which the proportions are reversed, and to low nickel contents of a few per cent. in high-tensile brasses and the like.

It would not be appropriate here to catalogue the uses of nickel. I pointed out earlier that nickel was a versatile alloying element, as a result of which it is to be found playing an important part in conjunction with most of the well-known metals. It is to be found alike

in hard magnetic alloys, in soft magnetic alloys, and in non-magnetic materials. It provides alloys of high, low, and even zero coefficient of expansion. It has its function in the hardest and the softest steels and iron. It may be found alloyed with gold and with lead, with tungsten and with aluminium, with chromium and copper and cobalt, with molybdenum and manganese, but it does its work in disguise—this unseen friend.

## 47th ANNUAL MAY LECTURE

# TECHNOLOGICAL HUMANISM \*

1775

By SIR ERIC ASHBY,† D.Sc., Sc.D., LL.D., D.I.C.

My first duty is to express gratitude to the Council for inviting me to deliver this lecture. My second duty is to explain to this audience why I accepted the invitation, for it is no light matter to take one's place in the galaxy of May lecturers. Nearly all my predecessors have been masters in the physical sciences or in engineering. I am a biologist who has turned to administration. My career could be regarded as one long disqualification for delivering a lecture before this Institute.

Nevertheless I accepted the invitation, because I believe that modern technology is confronting us with an exceedingly perplexing biological problem. It lies in the field of human ecology. It is the problem of how men and communities can adapt themselves to an environment which is changing with unprecedented speed.

Let me introduce the problem by way of an antithesis between technology and heredity. Napoleon, who died only 136 years ago, was not able to cross the Alps any faster than Hannibal crossed them. Today you can have breakfast in London and lunch in Rome. Gladstone, who died less than two generations ago, was not able to reach more people with his voice than Demosthenes reached with his. Today a Prime Minister's voice can be heard in the homes of millions. Sixty years ago a ship was out of touch with the world as soon as it lost sight of land. Today a ship can sail into the Arctic and remain as close to the news as a pedestrian in Piccadilly. The rate of change in the last hundred years is of a different order from that in previous centuries; and the changes are not merely advances in technology: they are drastic transformations in the environment of Man.

In contrast to this, Man remains very much as he was when history began. He learns no more efficiently than a pupil in Plato's Academy learnt. He thinks no more deeply than Plato thought. His chromosomes are conservative and resistant to change. He responds to new environments not by innovations in his heredity but by

the marvellous adaptability of his ancient genetic heritage. This adaptability would be impossible if the only channel of inheritance from one generation to the next were through the sperm and the egg. In Man—and in Man alone—there is a second channel of inheritance. The accumulated knowledge and traditions of Society are inherited not through the chromosomes but through education.‡ Education is the second channel of inheritance. Whether today's children will be able to cope with tomorrow's world depends largely on the inheritance of education which they receive. Over this channel of inheritance we have some influence and we can assume some responsibility; it is a responsibility which none of us would wish to escape, for not only are we the architects of this technological age: we are also the parents and grandparents of the children who have got to live in it.

This gigantic problem—the adaptation of Society to a rapidly changing environment—confronts teachers of all kinds at every level of education. In this lecture I shall focus on one thin layer of the problem, namely one aspect of the higher education of technologists. This is the concern of universities, colleges of technology, and professional institutes such as your own, and it is specially important because technologists are now becoming the pacemakers for social change; communities which formerly developed on the initiative of princes, or bishops, or financiers, or soldiers, now develop on the initiative of technologists. It is no exaggeration to say that the quality of education to be given to technologists may deeply influence the future of the West.

A great deal has been written recently about the desperate necessity to increase the annual output of technologists in Britain.§ This audience does not need to be reminded of this necessity. We are all of us persuaded that the quantity of technologists must be increased. What we are not at all clear about is the quality

\* Delivered at the Annual Spring Meeting, London, 29 April 1957.

† President and Vice-Chancellor, The Queen's University, Belfast.

‡ Education is here used in the widest sense, to cover the transmission of tradition and culture by instruction, precept, or imitation. The theme is as old as Plato. It has recently been

used with good effect by T. Dobzhansky, "The Biological Basis of Human Freedom", 1956: Oxford (Clarendon Press).

§ See, e.g., "Scientific and Engineering Manpower in Great Britain", 1956: London (H.M. Stationery Office) and "Engineering and Scientific Manpower in the United States, Western Europe, and Soviet Russia", 1956: Washington, D.C. (U.S. Government Printing Office).

of educational inheritance which technologists should receive. This lecture is concerned with quality, not quantity; what I propose to offer you in particular are some reflections on the content of education for higher technology in Britain. One warning before I begin: lectures on education are unlike lectures on metallurgy, for men have been thinking about education for over 2000 years, and some of their thinking never becomes out of date. Anything worth saying has already frequently been said. Anything hitherto unsaid should be regarded with the greatest suspicion.

It is first of all necessary to recollect how technological education arose in this country. The first Industrial Revolution was accomplished without scientists or technologists. Bramah and Maudslay, Arkwright and Crompton, the Darbys of Coalbrookdale and Neilson of Glasgow: these men had no systematic formal education in technology. While wars absorbed the energies and dissipated the capital of continental Europe, these men and others like them built up British industry until it had no rival in the world. Our industrial strength lay in our amateurs and our self-made men: the "cultivator of science" (as he was called), the craftsman-inventor, the mill-owner, the ironmaster. It was no accident that the Crystal Palace, that radiant symbol of the supremacy of British technology, was designed by an amateur. In 1851 most people in authority saw no danger in the fact that Britain had no state system of primary education (a third of the population was still unable to read or write); or in the fact that there was scarcely any science teaching in secondary schools ("it is plainly out of the question", said Moberly of Winchester, "that we should teach chemistry"); or in the fact that there were no opportunities for the study of higher technology except a little in London and in Scotland. It did not seem worth while to spend money on popular education, for industry was flourishing and manpower was cheap; nor did there seem to be any reason why the well-to-do classes (who were concerned with administration and management and not with mere technical details) should depart from their traditional education in the classics. Notwithstanding the Industrial Revolution, science and technology still played practically no part in higher education. Not long before the 1851 Exhibition the professors of physics and chemistry in Oxford had asked to be excused from lecturing altogether because there were so few students; and although the Cambridge science tripos was established in 1851, there were on the average only about nine successful candidates a year for the first twenty years.\*

Fortunately there were men of foresight who were unhappy about this situation. The Royal Commission on Oxford University tried to encourage Oxford to pay attention to the physical sciences by saying that unless "the clergy and gentry . . . are encouraged to keep pace with the progress of Society at large . . . they may find themselves placed below persons in many respects inferior and an opposition may arise between Physical Science and other branches of knowledge".† The

Royal Commission on Cambridge University was even more precise: "It may be quite true", the Report says, "that many of the practical . . . details of civil engineering may be best learned in the offices of engineers . . . but the knowledge of mathematics and of mechanical principles, as involved in the estimate of . . . the effects of elasticity, and generally of the operation of forces and pressures is so necessary . . . that no amount of practical skill and experience can ever replace the want of this theoretical knowledge."‡

These admonitions, and many others like them, made very little impression on the managers and mill-owners and ironmasters of Britain; these men were prepared to agree that science and technology were appropriate subjects for artisans and the lower middle class, but not for their own sons. And so, when the Society of Arts and the new government Department of Science and Art did set up schemes to encourage scientific education, these schemes were almost exclusively for the benefit of artisans and the "labouring poor". Clearly admonitions were not enough; a much more powerful impact was needed to overcome public inertia to technological education.

That impact was provided by the International Exhibition held in Paris in 1867. Britain had won awards in nearly every class in the 1851 Exhibition, but in the 1867 Exhibition she had to be content with a bare dozen awards. No longer was there the reassurance of easy industrial supremacy. Instead there was alarming evidence that Britain had made little progress in the peaceful arts of industry since 1851 and that Continental countries had now become very serious competitors.§ For example, a building was being put up at Glasgow with iron girders from Belgium, and it was asserted by Lyon Playfair that Belgian girders were cheaper because the Belgians had introduced economies depending on chemical analysis of the ore and limestone and fuel. British fabrics were being sent to France to be dyed on the ground that the French had techniques superior to our own. The French explained this by saying "the foreigner thinks it is our water and our sunshine, but we say it is our chemistry".||

What had happened in the interval between the two Exhibitions to bring about this change? There were many causes at work, but the chief cause undoubtedly arose from Britain's monopoly of much of the "know how" she had acquired during the Industrial Revolution. Up to 1825 it was a penal offence to enlist English artisans for employment abroad. Well on into Queen Victoria's reign, the export of spinning machinery to foreign countries was prohibited. When Continental countries began to build railways and mills and factories, they found it extremely difficult to obtain access to British techniques and practices. They had to make up for half a century of lost time. Their response was to produce a new species of professional man: the manager-technologist. To this end they established polytechnics with the specific purpose of training not the rank and file of workers, but engineers, designers, chemists, and potential managers for industry. In Zürich, in Dresden, in Delft, even in

\* Some interesting information on this and related topics has recently been assembled by D. S. L. Cardwell, "The Organization of Science in England". 1957: London (Heinemann).

† "Report of the Royal Commission on the University of Oxford." 1852.

‡ "Report of the Royal Commission on the University of

Cambridge." 1852.

§ Letter from Dr. Lyon Playfair to the Rt. Hon. Lord Taunton. *J. Soc. Arts*, 1867, 15, 477.

|| "Report of the Select Committee on Scientific Instruction," 1868.



the United States, there arose in mid-century technological institutes which had no parallel in Britain. Their function is well summarized by the words used to describe the Massachusetts Institute of Technology (founded in 1864) as a place "intended for those who seek administrative positions in business . . . where a systematic study of political and social relations and familiarity with scientific methods and processes are alike essential". In addition, almost every manufacturing town on the Continent had its continuation school where workers were obliged to extend their education up to the age of 16 by part-time day-release. And beside these there were specialist technical schools such as the Metallurgical School in Bochum (in Rhine-Westphalia), where potential managers and supervisors in the local factories and mines were released from industry for three years' full-time study.\*

The prime purpose of this widespread system of technological education abroad was not humanitarian: it was to enable Continental countries to catch up and to overtake British industry. Accordingly in the polytechnics emphasis was laid on a combination of science, technology, and general knowledge, suitable for men who would direct technical policy. Already by 1867 this experiment had begun to yield results. The results were obvious to Britain, and it was this challenge from the Continent, rather than a demand from industry at home, which drove Britain finally to set her educational house in order.

The leeway to be made up was truly appalling. Continental countries like Prussia had enjoyed compulsory primary education and compulsory further education with day-release for over a generation; and for years the *Real-schulen* of Germany had made science an integral part of secondary education. England in 1867 had no State school system, primary or secondary, and no general compulsory education. Continental universities were generously financed by the State, and many of them had well-established laboratories in close touch with industry. Bunsen in Heidelberg, Kekulé in Bonn, Liebig in Munich, Wöhler in Göttingen: all these chemists were training men who were accepted for industrial posts. England in 1867 was contributing scarcely any money by way of public funds to her universities, and her universities were contributing scarcely any technologists to industry. Per head of population, England had only about a quarter of the number of students Germany had. There was no Clarendon Laboratory in Oxford nor Cavendish Laboratory in Cambridge. Owens College in Manchester, sixteen years after its foundation, had only 113 students. Efforts of the Prince Consort to establish an industrial university in London had up to that time failed.

Because of this leeway, England could not meet the challenge from the Continent by building polytechnics; for she had no adequate foundation of schooling on which to build. And so, even after the need for technical and technological education had been realized, the response was slow and uncertain. In 1870 the Government introduced compulsory primary education. But Parliament was still unwilling to support trade schools and technical schools; it was the Livery Companies which first under-

took to assume this responsibility. In 1867 they set up the City and Guilds Institute, which fathered not only the first genuine technical college (at Finsbury) but (at South Kensington) the first genuine institute for higher technology. Not until 1889 did public authorities take over elementary technical education, and even then education in higher technology was not made a public responsibility; most of it was left to the universities and university colleges.

Here—in my opinion—is one clue to an understanding of our present curricula in higher technology. The spur to technological education in universities was not in the first instance a demand from industry for scientifically trained managers; it was the determination of a few far-sighted men to create a supply in anticipation of a demand. Accordingly, the pioneers of technological education in universities found themselves having to justify their subject on academic and not utilitarian grounds. They could not prove to their academic colleagues that higher technology was useful, and so they had to make it appear respectable. Accordingly they felt obliged to follow the fashions set by more venerable faculties. (Even as late as 1861 the University of Glasgow, which claims to have the oldest university chair of engineering in the Kingdom, did not consider engineering to be "a proper department in which a degree could be conferred", and it remained for years in the Faculty of Arts.) Therefore when, under the influence of German scholarship, specialization became fashionable, technology followed the fashion. Part of the price paid for following the fashion was a narrowing of the curriculum in every discipline—not only in technology. No longer was it necessary for a man taking the classical tripos at Cambridge to pass first a tripos in mathematics and mechanics. No longer did the London B.A. require some knowledge of both the humanities and the sciences. The universities assumed (and with some justification in those days) that secondary schools would provide a balanced general education and that universities could concentrate on turning their best men into experts: experts in classical philology, or history, or chemistry. Where the arts and sciences led, technology followed, and the trend in higher technological education was consistent with the pattern of British industry. In Continental countries, many technological experts found themselves in the board-room, or acting as administrative civil servants. Their education prepared them for these responsibilities. In Britain administration and policy-making remained largely in the hands of men with no technological training. The chemist from Roscoe's laboratory in Manchester or from Graham's laboratory in London might look forward to a career in industry as a chemist. But there was no great demand from industry to equip him to manage, or to be responsible for human beings. Higher technological education abroad was from the beginning intended to produce not only experts but also managers and leaders in industry. In the British economy of the 1860s and 1870s, there was no shortage of men for the board-room: the shortage was in the design office, the laboratory, and the plant; therefore the pattern of higher technological education set in this country at that time was one to produce experts to advise

\* A description of this metallurgical school is given in the "Second Report of the Royal Commission on Technical Instruction", 1884, p. 117.



on policy, not leaders to make policy. With modifications, accretions, and improvements, that pattern has persisted ever since.

This long historical digression enables us to diagnose the present state of higher technological education in Britain. On the one hand, there are grounds for satisfaction: there is no reason to believe that any foreign university can teach the practice and techniques of science and technology better than they are taught in such places as Imperial College or Manchester or Cambridge. Regarded as a preparation for doing nothing but organic chemistry, or non-ferrous metallurgy, or light electrical engineering—in other words, regarded as a production line for highly differentiated experts—there is nothing much wrong with technological education in Britain. On the other hand, grounds for anxiety do exist, for buried at the foundations of our system for educating higher technologists there are two assumptions, both of which are wrong. The first assumption is that the technologist has had a balanced schooling with a thorough grounding in what are vaguely called “the humanities”. This assumption may have been justified fifty years ago.\* Today it is no longer justified. The would-be technologist has had to decide in his early teens to go up the school on the science side and not on the classical side, and he has to specialize for ever afterwards. No secondary education is so overspecialized as ours in Britain today. The second assumption is that the technologist is to become and to remain an expert to serve the manager, never to become a manager himself. This assumption, also, is no longer justified; and in the Second Industrial Revolution, which is upon us now, it will become an utterly obsolete assumption. Because these two assumptions are still made, the question of including the humanities in higher technological education is still not taken seriously. True, it is a subject worn threadbare in graduation addresses, educational conferences, and academic pamphleteering, but (with one or two exceptions) it has not yet become the subject for faculty decisions or senate resolutions. Ask professors of technology what they are doing about it, and they reply that the curriculum is already overloaded, and nothing more can be added. Ask the advice of arts professors, and some of them will reply that a faculty of arts is not a faculty of culture; it has no contribution to offer toward civilizing the “savage technologist”. The historian (they say), pursuing his minute enquiries into mediæval charters, has no more relevant contribution to make to technological education than the biologist has, assiduously analysing the urine of mice. There are, you see, resistances from both sides: faculties of technology cannot find room for the humanities; faculties of arts—in this context at any rate and if we are to believe some arts professors—do not regard themselves as trustees responsible for communicating the values and traditions of Western civilization to other faculties.

Contrast this with the training being given to technologists in other countries. I quoted just now the purpose of the Massachusetts Institute of Technology: to train

men for posts where “a systematic study of political and social relations and familiarity with scientific methods and processes are alike essential”. The student at the Massachusetts Institute of Technology must devote a considerable portion of his time throughout all four years of his course to English composition and literature, history, psychology, international relations, and economics; and these subjects are taught in a way which is relevant to technologists. In the Swiss Federal School of Technology at Zürich, third- and fourth-year students include in their course law, economics, and management, and there is a Department of General Education with twelve professorships covering foreign languages, philosophy, history, law, and political economy. All students must register for at least one course in this Department. In the Technical University of Delft, there is a so-called *Studium Generale*, which provides lectures on religion, philosophy, music, and art; something similar was already being done there over 70 years ago, in the 1880s. Even technological institutions in the Soviet Union devote some time to the humanities and the social sciences.† The British Commonwealth has not ignored these examples: in the New South Wales University of Technology, there is a Department of Humanities, with a full professor at its head. Even some English technical colleges have introduced an element of the humanities into their courses.‡ Nevertheless, universities in Britain are not yet persuaded that the humanities are an essential ingredient in higher technological education. Many universities do indeed arrange opportunities for students to broaden their interests through voluntary attendance at lectures on art and music and the like. This is admirable, but it is a very different thing from recognizing certain humanistic studies as an integral part of a technologist’s formal higher-education.

At this stage I must ask you to accompany me into another digression. It is a thankless task to define the humanities, but when I talk about including the humanities in higher technological education, there must be no doubt about which humanities I mean. I do not mean courses on the appreciation of poetry or music or pictures. In my experience the student who whistles Bartok or reads Dylan Thomas or buys a Picasso reproduction for his room has come to care for these artists without any help from formal university courses. That sort of appreciation we can safely leave to the students themselves (although we should certainly encourage it in every way we can); it is just as likely to appear among students of technology as among arts students. (In fact, there’s something to be said for not being an arts student if you care for literature, because you then avoid the earnest but misguided species of arts don who believes that a student cannot read “Anna Karenina” or “King Lear” or “The Turn of the Screw” unless some university teacher has first interposed himself between the student and Tolstoy or Shakespeare or Henry James, to deaden the impact of genius by explaining what these writers really intended to say to their readers.) We can safely

\* And not only in the humanities: it is now forgotten that the “Sixth Report of the Royal Commission on Scientific Instruction” (1872–75) recommended unanimously that in all public and endowed schools six hours a week should be devoted to science and that science should constitute one-sixth of the leaving examination. Such a recommendation would today be regarded as

unreasonable by most secondary schools. It is important to recollect that the curriculum in most secondary schools today is much less balanced than it was nearly three generations ago.

† See N. de Witt, “Soviet Professional Manpower”. 1955: Washington, D.C. (National Science Foundation).

‡ “Liberal Education in a Technical Age.” 1955: London.



disregard the sentimentalists who say that faculties of technology fill the minds and starve the souls of the young. There is no evidence that the souls of technologists are starved. There is evidence—as I hope to persuade you—that the minds of most technologists are deficient in certain arts subjects needed for their professions.

So let us be quite hard-headed about the humanities which should be included in higher technological education. There are four criteria for selecting them. First, they should not include subjects which can and ought to be taught at school. Second, they should be taught as genuine humanities, that is to say they should deal with the creative and social acts of Man, and particularly with value-judgements about these acts: Man's ideas of right and wrong, of good and evil, of justice, freedom, and government. Third, they should be taught in such a way as to be relevant to the contemporary world and to technology. (This does not mean we have to invent newfangled humanities: nothing could be more relevant to the contemporary world than parts of Aristotle's "Politics".) Fourth, humanities at this level of teaching should be instruments to enhance the individuality of students, to resist that levelling of differences in taste and personality, that tendency to increase social entropy, which is a melancholy consequence of the modern techniques of mass communication.

Indeed, what is needed is nothing less than a revision of the idea of a liberal education. The *Oxford Dictionary* defines liberal education as education fit for a gentleman. That is still an acceptable definition; it is the idea of a gentleman which has changed. A century ago, when Britain awoke to the need for technological education, a gentleman belonged to what was called the leisured class. The occupations of his leisure did not require any knowledge of science or technology. Modern gentlemen do not belong to the leisured class. Many of them work something like a seventy-hour week, and more and more of them are finding that their business requires expert knowledge. Even members of the House of Lords find themselves called upon to make decisions about radioactive fall out, and overheating during supersonic flight, and the strontium content of bones. Ministers and senior civil servants have to deal with highly technical policy in D.S.I.R. and the Ministry of Supply. Even such a gentlemanly subject as the state of the River Thames cannot be understood without some knowledge of oxidation and reduction, detergents, and the biochemistry of sewage. Dare I suggest, in this audience at any rate, that in order to be a gentleman nowadays, one has to be something of a technologist?

But technology alone will not make a modern gentleman. And this brings me to the core of my lecture. It is nothing new to suggest that technologists should know something of the humanities. I want to go farther; I want to suggest that, for the gentleman technologist, certain of the humanities are an integral part of technology. "Technological humanism" is not just a rhetorical phrase: it has genuine content.

For technology is inseparable from men and communities. In this respect technology differs from pure science. It is the essence of the scientific method that the human element must be eliminated. Contrary to the assumptions of some people, science does not dis-

pense with values; but it does eliminate the variability of human response to values. It concerns itself only with phenomena upon which all qualified observers agree. It describes, measures, and classifies in such a way that variation due to human judgment is eliminated.

Unlike science, technology concerns the applications of science to the needs of man and society. Therefore technology is inseparable from humanism. The technologist is up to his neck in human problems whether he likes it or not. Take a simple example: the civil engineer who builds a road into a new territory in tropical Africa. He may assert that it is not his business to take into account the effect his road will have on primitive villages up-country; but his road is in fact a major experiment in social anthropology. He does not need to be a professional anthropologist, but he cannot afford to be utterly ignorant of the implications of his work. He is a technologist, not a pure scientist: the social consequences of his work are therefore an integral part of his profession. Take another example from one of the most ancient technologies: medicine. Chemotherapy and preventive medicine and contraceptives between them have enormously altered the pattern of family life. The next generation will inherit from us a surplus of elderly people. This situation sets problems which have given rise already to a new subject called gerontology. Now the problems of gerontology are not merely scientific; they involve some of the perennial issues of humanity—family affection, group loyalty, and social justice. The practitioner in social medicine is a technologist: he cannot repudiate these involvements.

Long ago, in "Science and the Modern World", A. N. Whitehead saw the essential unity between technology and humanism. Listen to what he said:

"A factory with its machinery, its community of operatives, its social service to the general population, its dependence upon organizing and designing genius, its potentialities as a source of wealth to the holders of its stock is an organism exhibiting a variety of vivid values. What we want to train is the habit of apprehending such an organism in its completeness."

*The habit of apprehending a technology in its completeness*: this is the essence of technological humanism, and this surely is what we should expect an education in higher technology to achieve. How is it to be achieved? Ninety years ago, when Thomas Henry Huxley was giving evidence before a Select Committee on Scientific Instruction, he poured scorn on the universities because they made literature and grammar the basis of education and (as he put it) "they actually plume themselves upon their liberality when they stick a few bits of science on the outside of the fabric". It will not do for us, ninety years later, to reverse the process and to plume ourselves upon our liberality when we stick a few bits of the humanities on the outside of the fabric of higher technology. That would not achieve our purpose; it would only generate in students a contempt for the humanities, analogous to the contempt which public schoolboys in the 1860s had for science. It is no good trifling with this problem. We must cut the path to a liberal education *through* a man's specialism, not by by-passing it for an hour or two a week.

It should be our business in higher technological education to persuade students that they cannot practise



technology without continually reflecting upon its social implications, and that some understanding of the humanities is essential to this reflection. For a metallurgist to take a course in general history in order to acquire a little culture is an innocent but not necessarily a very profitable amusement. But if the metallurgist studies the social and economic history of the Industrial Revolution; if he learns how the making of iron followed the forests across Europe until coal replaced charcoal; if he realizes how mining and the building of railways and canals stimulated the study of geology, and how this in turn brought men face to face with the evidence for organic evolution; if he considers the effect which the introduction of electric power has had on the distribution and lay-out of factories, and the effect which aluminium alloys have already had (through world transport) on the conduct of diplomacy: then history becomes integrated with metallurgy; his humanism becomes a relevant part of his day-to-day thinking. May I be allowed to quote to you a paragraph I have already published on this matter: \*

"Suppose a student decides to take up the study of brewing: his way to acquire general culture is not by diluting his brewing courses with popular lectures on architecture, social history, and ethics, but by making brewing the core of his studies. The *sine qua non* for a man who desires to be cultured is a deep and enduring enthusiasm to do one thing excellently. So there must first of all be an assurance that the student genuinely wants to make beer. From this it is a natural step to the study of biology, microbiology, and chemistry: all subjects which can be studied not as techniques to be practised but as ideas to be understood. As his studies gain momentum the student will naturally become interested in the economics of marketing beer, in public houses, in their design, in architecture; or in the history of beer drinking from the time of the early Egyptian inscriptions, and so in social history; or in the unhappy moral effects of drinking too much beer, and so in religion and ethics . . . It appears today as though technology will become the key to general culture. Technology: not science; because scientific systems are too self-contained—they exclude too many factors, including Man—whereas the technologist has to make something which requires as its ingredients not only science but an understanding of popular art and commerce, of psychology, something of morals and justice, and skill in the art of communication. A technologist who cannot weave his technology into the fabric of society is not first rate; a technologist who can weave his technology into the fabric of society can undoubtedly claim to have . . . general culture."

If these arguments are acceptable, the mischievous antithesis between specialization and general culture disappears.

I must not shrink from the last step. Anyone can blow bubbles about education for an hour. But educational bubbles have no value unless they can be stabilized; and the only stabilizers are curricula and time-tables. "Very well" (you will be saying) "what does all this involve in (for example) the weekly time-table of a civil engineer in a British University?"

I shall try to tell you. It involves a little more time in the undergraduate course, secured either by cutting some subjects down or by lengthening the course. Since Britain is about the last country in the world to

attempt to train technologists in three years from the post-intermediate stage, I would not regard this as a very grave obstacle. It involves a little more money. Since it costs £45,000 to train a bomber pilot † and about £1500 to train a technologist, I would not regard some additional cost as a grave obstacle either. It involves some newly designed courses which are within the capacity of lecturers normally to be found in faculties of arts, law, and economics.

Here are some examples of the choice of courses these lecturers might offer to technology students:

(a) A course on ethics and jurisprudence, with some discussion of the principles of law and justice (such as might be given by a legal philosopher).

(b) A course on industrial and social history of Europe since the seventeenth century, with emphasis on the social effects of technological change (such as is already offered at the Dutch Institute of Social Studies at The Hague).

(c) A course on political theory, political institutions, and the history of guilds and trade unions (this would be an opportunity for mediaeval as well as modern historians).

(d) A course on industrial psychology.

(e) A course on sociology and social anthropology.

(f) A course on the history of technology, including readings from the classics of science and technology (this might go some way toward meeting one criticism of all present courses on technology, namely, that it is possible to get a first-class honours degree without ever having read a work of genius).

(g) A course on linguistics and communication (a development of some of the material contributed to the Communication Research Centre at University College, London).‡

Not every student should take every course. It would be very much better that a student should pursue one rigorous course over a period of (say) two years (with the discipline of reading and essay writing and examination which should be required in such a course) than that he should ramble in a dilettante fashion among several courses. The courses would have to be prepared specifically for technologists, and it is important that they should be used as an opportunity for exercises in communication between students; for inarticulateness is an occupational disease among technologists; and it is a disease which I believe could be very much relieved by this simple prophylactic treatment.

Among the criticisms which are likely to be levelled against such courses as these, there is one criticism I wish to anticipate. Courses like these (it will be said) are not detailed enough to give the technologist mastery in any of these fields, but they may give him the illusion of mastery. It is not a serious criticism, for the same might be said of most university courses, particularly in the humanities: a student who has passed an examination in English usage has no right to consider himself a master of English prose. Nor, I think, is it a valid criticism, for it will have to be made clear that the purpose of the courses is not to train practitioners but to provide ideas

\* *Research*, 1955, 8, 419.

† *The Times*, 13 February 1957.

‡ "Studies in Communication." 1955: London (Secker and Warburg).



which will act as templates in the mind. On these templates the technologist can shape his own thinking from his own experience; without them he will be unable to comprehend his technology in its completeness.

"Liberality in education", Samuel Alexander once wrote, is "a spirit of pursuit, not a choice of subject." If technologists are to enter fully into their responsibilities in the world of tomorrow, they have to adapt themselves not only to novel technologies: they must also be able to adapt themselves to the social consequences of the novel technologies. Their prospects of adaptation certainly depend in part on the spirit with which they pursue technology as undergraduates. To pursue technology in a spirit of liberality, they need not only a thorough training in the theory and practice of technology (they get that already); they need also an understanding of men and communities such as is

acquired through literature and history and the social sciences.

Let me end by summing up in one minute what I have been trying to say for an hour. All industrial peoples have to solve a great problem in human ecology, namely how to adapt themselves, through the second channel of inheritance, to the social climate which is being created by modern technology. Technologists have a special responsibility to solve this problem for themselves and to reflect on its implications for their fellow citizens. I am persuaded that the solution for technologists lies through the inheritance of education they receive, and I am persuaded that the appropriate education for higher technology should be one which does for contemporary civilization what our traditional classical education has so successfully done for the civilizations of Greece and Rome.

# 1776 A NOTE ON THE METALLOGRAPHY OF CRACKING DURING CREEP \*

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## SYNOPSIS

Microspecimens of 57 test-pieces of certain commercial creep-resistant metals, namely Nimonic 80, Nimonic 80A, Nimonic 90, G32, and Rex 337A, broken in creep tests at various stresses and temperatures, have been examined in a study of the inception of fracture under different conditions. With the exception of Nimonic 80, few cracks in which were observed under the conditions of the tests, a clear picture emerged. The stress seems to be the main controlling factor. At low stress, fracture begins by the formation of isolated cavities lying mainly in transverse grain boundaries; at high stress, fracture starts with cracks which appear to be produced by relatively large stress concentrations. In Rex 337A these cracks lay inside the grains, often remote from grain boundaries, but in the other materials they were located at grain corners. The minimum stress needed to produce the cracks is sufficiently below the calculated minimum to suggest that cohesion in these alloys is lower than in pure metals. If so, the probable reason is that alloying elements or impurities reduce the surface energy.

## I.—INTRODUCTION

It used to be thought that intergranular cracks generated during creep always started at grain corners, but it has recently been shown<sup>1</sup> that cavities, which unite to form cracks, may form at any point along a grain boundary. It seemed that the explanation of this apparent contradiction might be that the starting point of a crack depended on the conditions of test, and the present work was carried out to examine this possibility.

## II.—EXPERIMENTAL DETAILS

The materials studied were certain commercial creep-resistant metals, creep tests on which had already been made over a range of stresses and temperatures. From each specimen, a longitudinal section at the fracture was cut, polished, and etched. It was essential to polish and etch several times to reveal the cracks properly. After the first polish, hair-line cracks were often visible, which invariably opened out during repeated polishing and etching (or electrolytic polishing). Even in these hard metals, the crack edges must have become burred over during grinding, so closing up the mouth of the crack.

To study the origin of cracks, it is necessary to examine them while they are still small, since the origin is not so clearly ascertainable when, for example, the whole length of a grain boundary has parted. In all specimens in which many cracks were found, cracks small enough for this purpose occurred within 1 cm. of the fracture. The smallest cracks definitely identifiable measured about 1  $\mu$  across. Some of the specimens contained numerous inclusions comparable in size with small cracks; these dissolved on etching, leaving holes. The criterion

adopted for distinguishing a crack from such a feature was whether or not the latter eventually disappeared on moving away from the fracture. Sometimes it was necessary to take a section from the relatively unstrained shoulder of the test specimen to settle this point. Besides the smallest definitely identifiable holes of about 1  $\mu$  dia., other smaller dark spots were seen, which might have been holes and which satisfied this criterion. However, these were not numerous, so that even if they were holes they did not affect the average, and the smallest common size was still about 1  $\mu$  across.

## III.—RESULTS ‡

### 1. NIMONIC 90

The composition of this material is given in Table I.

TABLE I.—Composition of Nimonic 90.

Mark	C, %	Si, %	Mn, %	Cr, %	Co, %	Fe, %	Ti, %	Al, %	Cu, %	Ni, %
RSN	0.04	0.6	0.4	20	20	0.4	2.5	1.0	not detd.	balance
Solution-treated 8 hr. at 1150° C., air-cooled, aged 16 hr. at 700° C., air-cooled										
TPA	0.07	0.5	0.13	20	20	0.4	2.5	1.5	0.1	balance
Solution-treated 8 hr. at 1080° C., air-cooled, aged 16 hr. at 700° C., air-cooled										

Details of tests on the specimens and results of the micro-examination are given in Table II. These show that the minor differences in composition and heat-treatment between the two batches had no obvious effect.

\* Manuscript received 27 December 1956.

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‡ The test results reported on proprietary alloys are not

necessarily representative of material now being produced. Before such data are used for design purposes, the firm manufacturing the alloy should be consulted.



From the microspecimens it was clear that nearly all the fractures followed an almost entirely intergranular path, that cracking occurred preferentially along grain boundaries transverse to the applied stress, and that both the types of initial crack or cavity referred to in the Introduction occurred, the test conditions determining which

TABLE II.—Experimental Data Relating to Nimonic 90 Specimens.

Mark	Test Temp., °C.	Stress, tons/in. <sup>2</sup>	Time to Fracture, hr.	Elongation	Pre-dominant Type of Cavity *	Pre-dominant Type of Fracture †
RSN 8C3	700	32	80-47	...	a	ig
" 7C2	700	18	5692	...	a	ig
" 14C1	750	24	64	2%	a	ig
" 35C3	750	10½	8636	2.4% on 2½ in.	a + b	ig
" 4C3	800	12	482½	...	a	ig
" 4C2	800	8	2739	...	a + b	ig
" 15C3	815	16	42	7% on 2 in.	a	ig
" 30C3	815	6	4493	2½% on 2 in.	b	ig
TPA 3C1	850	15	12½	4½% on ¼ in.	a + b	ig
RSN 35C1	850	10	72½	6½% on ¼ in.	a + b	ig
TPA 4C2	900	10	10	12½% on 2 in.	a	ig
" 6C3	900	2½	1900½	8½% on ¼ in.	b	ig
" 10C1	950	5	7½	23% on 2 in.	b	ig
" 11C2	950	4	60	...	b	Some parts ig Some parts ig
RSN 36C2	950	3	169	...	b	Some parts ig Some parts ig
TPA 3C3	1000	2	15	93% on 2 in.	No small cracks	ig

\* Type *a* are wedge-shaped cavities based on a grain corner (Fig. 1, Plate LXXIV). Type *b* are isolated cavities occurring anywhere along a boundary (Fig. 3, Plate LXXIV).

† *ig* = intergranular fracture; *ig* = transgranular fracture.

one predominated in any particular specimen. Wedge-shaped cracks based on a grain corner (type *a*) predominated in specimens tested at high stress (Fig. 1, Plate LXXIV). As suggested by Zener<sup>2</sup> and by Eborall,<sup>3</sup> this kind of crack can reasonably be ascribed to the stress concentration set up at the grain corner by the relative sliding between the grains, an interpretation supported by the fairly frequent appearance of cracks at both ends of a sliding boundary, as in Fig. 2 (Plate LXXIV). Rows of rounded cavities, resembling particles of dark precipitate (Fig. 3, Plate LXXIV), predominated in specimens tested at low stress. This kind of incipient cracking is referred to as type (*b*). Fig. 3 depicts a typical region some distance from the fracture, where the cavities presumably formed later than at places near the fracture. On proceeding from the region of Fig. 3 towards the fracture, it is easy to see that these cavities coalesced (Fig. 4, Plate LXXIV) until the whole length of a grain boundary had parted (Fig. 5, Plate LXXIV).

In specimens containing predominantly type-(*b*) cavities, the large cracks had wavy edges (Fig. 5), which evidently outlined the original cavities, whereas in specimens containing predominantly type-(*a*) cracks the edges lacked this large-scale waviness (Figs. 1 and 2). It was thus possible to tell from the appearance of fairly large cracks whether they were originally of type (*a*) or type (*b*). This also applied to the other materials examined. However, the distinction between type (*a*) and type (*b*) was always based, as mentioned earlier, on an examination of cracks at an early stage in their development.

To make these remarks more quantitative, the pre-dominant type of incipient crack in Nimonic 90 is depicted on a stress/temperature diagram in Fig. 9. In some specimens, for a middle range of stress, both kinds

were general, but below about 7 tons/in.<sup>2</sup> few or no type-(*a*) cracks were seen, whereas above 15 tons/in.<sup>2</sup> there were few or none of type (*b*). This means that below 7 tons/in.<sup>2</sup> type-(*a*) cracks form more slowly than type (*b*); the latter have time to coalesce and presumably cause fracture before many type-(*a*) cracks have appeared. Raising the stress gradually reverses this situation, and above 15 tons/in.<sup>2</sup> type-(*a*) cracks cause fracture before many of type (*b*) are visible.

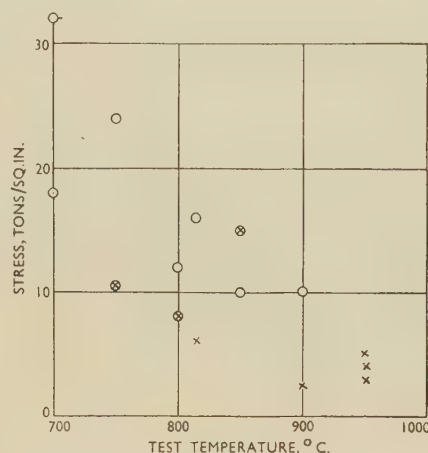


Fig. 9.—Types of Cavity Found in Nimonic 90 at Different Stresses and Temperatures.

#### KEY

- Wedge-shaped crack based on a grain corner (type *a*).
- × Separate cavities occurring at any point along grain boundaries (type *b*).
- ⊗ Mixture of types *a* and *b*.

## 2. NIMONIC 80A AND 80

Table III gives the composition of this material.

TABLE III.—Composition of Nimonic 80A and 80.

Mark	C, %	Si, %	Mn, %	Cr, %	Fe, %	Ti, %	Al, %	Cu, %	Ni, %
SMW (Nimonic 80A)	0.082	0.33	Not detd.	18.8	0.20	2.41	1.10	Not detd.	76.3
SOK (Nimonic 80)	0.03	0.31	0.05	19.16	0.27	2.09	1.02	0.07	balance

Solution-treated 8 hr. at 1080° C., air-cooled, aged 16 hr. at 700° C., air-cooled

Details of tests on the specimens and results of the micro-examination are given in Table IV.

The behaviour of Nimonic 80A resembles that of Nimonic 90 in that type-(*b*) cavities form at low stress and type-(*a*) cavities at high stress. The minimum stress required for the formation of type-(*a*) cavities is about 15 tons/in.<sup>2</sup>, and is thus much higher than for Nimonic 90. Detailed comparison of the data in Tables II and IV shows that this is due at least in part to the more rapid formation of type-(*b*) cavities in Nimonic 80A. For example, the Nimonic 90 specimen tested at 10½ tons/in.<sup>2</sup> and 750° C. broke after approximately 9000 hr. and contained both (*a*) and (*b*) types, whereas the Nimonic 80A specimen tested under similar conditions broke in one-third the time and contained only type-(*b*) cavities; their development had therefore been sufficiently faster to cause fracture in the shorter time.

The Nimonic 80 specimens contained only one or two cracks close to or joined to the fracture surface, and no attempt was made to draw conclusions from them.

TABLE IV.—*Experimental Data Relating to Nimonic 80A and 80 Specimens.*

Mark	Test Temp., °C.	Stress, tons/in. <sup>2</sup>	Time to Fracture, hr.	Elongation	Pre-dominant Type of Cavity *	Pre-dominant Type of Fracture †
<i>Nimonic 80A</i>						
SMW 80C2	700	35	19½	3½% on 2 in.	<i>a</i>	Mainly <i>tg</i>
" 50C2	700	28	161½	4½% on 2 in.	<i>a + b</i>	<i>tg + ig</i>
" 60C3	700	20	1217	1½% on 2 in.	<i>b + a</i>	<i>tg + tg</i>
" 10C2	700	15	4584	2% on 2½ in.	<i>b + a</i>	<i>tg + tg</i>
" 80C3	750	24	23½	6½% on 2 in.	<i>a + b</i>	<i>tg</i>
" 60C2	750	20	98½	8% on 2 in.	<i>a + b</i>	<i>tg + ig</i>
" 110C3	750	10	3110	2% on 2 in.,	<i>b</i>	<i>tg + tg</i>
				4½% on $\sqrt[3]{A}$		
" 120C2	815	15	26½	6½% on 2 in.	<i>a + b</i>	<i>tg + tg</i>
				11% on $\sqrt[3]{A}$		
" 9C2	815	4	4275	Not measurable	<i>b</i>	<i>ig + tg</i>
" 17C1	1000	2	23½	85% on 1.65 in.	Uncertain	Uncertain
" 16C2	1000	1	199	51% on $\sqrt[3]{A}$	<i>b</i>	"
<i>Nimonic 80</i>						
SOK 20C2	650	26	331	1½% on 2½ in.	<i>a</i>	Mainly <i>tg</i>
" 30C1	700	20	234½	1% on 2 in.	Very few	" <i>tg</i>
" 20C1	700	18	673	1½% on 2 in.	"	" <i>tg</i>

\* See footnotes to Table II.

### 3. G32 ALLOY

The composition of this material was Co 48, Cr 20, Fe 13, Ni 11, V 2.5, Mo 2.3, Nb 1.3, Mn 0.8, Si 0.4,

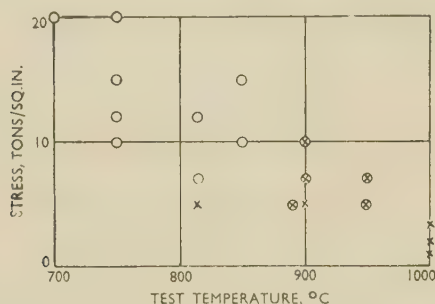


FIG. 10.—Types of Cavity Found in G32 at Different Stresses and Temperatures. Key as for Fig. 9.

C 0.3%. It was received solution-treated and aged by the makers and was tested in that condition. Details of the tests and results of the micro-examination are given in Table V.

The cracks in these specimens exactly resembled those in the Nimonic 90 specimens. The predominant type of cavity is indicated on a stress/temperature diagram in Fig. 10, from which it can be seen that stress has the same effect as in Nimonic 90; type-(*a*) cracks become rare below about 5 tons/in.<sup>2</sup> and type-(*b*) cracks rare above about 10 tons/in.<sup>2</sup>.

In one specimen (RYS 1C1), a few rows of cracks were seen parallel to the length axis. Presumably the cause is inhomogeneous composition of the metal.

### 4. REX 337A

The nominal composition of this material was: C 0.18, Si 0.6, Mn 0.6, Ni 18, Cr 14, Cu 4, Ti 0.8, Mo 4, Co 7%, Fe balance.

It was received in a heat-treated condition (solution-treated at 1230° C. followed by ageing at 700°–750° C.) and tested in that condition.

Table VI includes particulars of tests on the specimens and results of the micro-examination.

TABLE V.—*Experimental Data Relating to G32 Specimens.*

Mark	Test Temp., °C.	Stress, tons/in. <sup>2</sup>	Time to Fracture, hr.	Elongation	Pre-dominant Type of Cavity *	Pre-dominant Type of Fracture †
RYS 1C1	700	20	174	...	<i>a</i>	<i>ig</i>
" 20C2	750	20	5½–21½	12½%	<i>a</i>	<i>ig</i>
" 20C1	750	15	609	...	<i>a</i>	<i>ig</i>
" 30C2	750	12	3,472	14%	<i>a</i>	<i>ig</i>
" 10C2	750	10	8,354	11½%	<i>a</i>	<i>ig</i>
" 21C1	815	12	213½	7½% on 2 in.	<i>a</i>	<i>ig</i>
" 22C1	815	7	2,046½	16½% on 2 in.	<i>a</i>	<i>ig</i>
" 33C1	815	5	12,336	11% on 2½ in.	<i>b</i>	<i>ig</i>
" 30C2	850	15	4	13% on 2 in.,	<i>a</i>	<i>ig</i>
				16% on $\sqrt[3]{A}$		
" 48C1	850	10	120	12% on 2½ in.,	<i>a</i>	<i>ig</i>
				15.7% on $\sqrt[3]{A}$		
" 50C2	890	10	22	14% on 2 in.	Cracks too few to be sure	<i>tg + ig</i>
" 44C2	890	5	752	10% on 2 in.	<i>a + b</i>	<i>ig</i>
" 20C2	900	10	12	12% approx. on 2 in.	<i>a + b</i>	<i>ig + tg</i>
" 52C2	900	7	107	10½% on 2 in.	<i>a + b</i>	<i>ig</i>
" 52C1	900	5	507½	8% on 2 in.	<i>a + b</i>	<i>ig</i>
" 58C2	950	7	7½	...	<i>a + b</i>	<i>ig + tg</i>
" 58C1	950	5	52½	11% on 2 in.	<i>a + b</i>	Mainly <i>ig</i>
" 310F	1000	3-12	26½	2% approx. on 1.14 in.	<i>b</i>	<i>ig</i>
" 56C1	1000	2	116½	...	<i>b</i>	Uncertain
" 55C2	1000	1	427½	8% on 1½ in.	<i>b</i>	Some parts <i>ig</i>

\* See footnotes to Table II.

TABLE VI.—*Experimental Data Relating to Rex 337A Specimens.*

Mark	Test Temp., °C.	Stress, tons/in. <sup>2</sup>	Time to Fracture, hr.	Elongation	Pre-dominant Type of Cavity *	Predominant Type of Fracture †
RTE 70C6	700	20	1½	14% on 2 in.	<i>a + b</i>	<i>ig</i>
" 7C5	700	16	29	13½% on 2 in.	<i>a + b</i>	<i>ig</i>
" 10C4	700	11	3393	...	<i>a + b</i>	Indeterminate
" 60C1	750	15	5	9½% on 2 in.	<i>a + b</i>	<i>ig</i>
" 60C2	750	10	485	4½% on 2 in.	<i>a + b</i>	<i>ig</i>
" 6C5	750	8	4076	...	<i>a + b</i>	<i>ig + tg</i>
" 8C5	750	7	9171	...	<i>b</i>	<i>ig</i>

\* † See footnotes to Table II.

† These are cracks, presumably caused by a stress concentration, but which occur either wholly in the grain interior (as at high stress) or (as at intermediate stress) have one end touching a grain boundary, or cross a grain boundary, or lie partly in a grain boundary (Fig. 6, Plate LXXIV).

At low stress, type-(*b*) cavities, exactly the same as those in Nimonic 90 or in G32, occurred. At the highest stress, however, most of the cracks lay entirely in the grain interior, as shown in Fig. 6, and at a rather lower stress the cracks looked much the same, though they often touched a grain boundary.

These grain-interior cracks will resemble the type-(*a*) cracks found in Nimonic 90 and G32 if they are the result of stress concentrations set up by slip inside the grains. Some evidence that this is the case was found in specimen RTE 6C1. On etching striations became visible which were apparently slip bands; these striations sometimes led into a crack, but did not continue on the other side. An example is shown in the specimen in Fig. 8 (Plate LXXIV), slip in which could not proceed beyond the central crack because the latter was bounded on the



upper side by a hard particle which would stop slip; consequently, if the slip shown coming into the crack from the upper right direction occurred before the crack was formed, a stress concentration would have been produced on the right-hand side of the particle and may have generated the crack in the way Mott<sup>4</sup> and Stroh<sup>5</sup> have suggested. There are also other slip lines leading into the crack from the top right, so that two sets of slip bands may have co-operated in producing a crack in the way suggested by Kochendörfer<sup>6</sup> and by Fisher.<sup>7</sup>

If this is so, the effect of stress on type of crack is similar to that operating in Nimonic 90 and G32, and the minimum stress below which type-(a) cracks are not produced is 7 tons/in.<sup>2</sup>.

Corresponding to the change in location of the cracks from grain interior to grain boundary as the stress was decreased, the fracture path changed from transcrystalline to intercrystalline.

The temperature range (700°–750° C.) over which tests were made was too small to be certain whether temperature had a systematic influence on crack type or location, but the proportion of grain-boundary cracks was higher in RTE 6C2 (10 tons/in.<sup>2</sup>, 750° C.) than in 1C4 (11 tons/in.<sup>2</sup>, 700° C.), and in 6C1 (15 tons/in.<sup>2</sup>, 750° C.) than in 7C5 (16 tons/in.<sup>2</sup>, 700° C.). As far as these results go, a rise in temperature increases the likelihood of cracks occurring at grain boundaries instead of inside grains.

In RTE 7C5 a few longitudinal rows of cracks were seen similar to those in the G32 specimen RYS 1C1.

#### IV.—DISCUSSION

The appearance of a type-(b) cavity, or a row of type-(b) cavities, could clearly be produced by suitably sectioning a type-(a) crack whose forward edge was sufficiently irregular, i.e. looking in plan like the fingers of a hand, in which case there would be little significance in the distinction between types (a) and (b). But the gradual change with decrease in stress from practically wholly type (a) to practically wholly type (b), seems to exclude this interpretation. If all cracks were really of type (a) and the type-(b) appearance was due simply to a particular manner of sectioning some of them, the others should still present a type-(a) appearance on the section, and plenty of these would be seen in all specimens. However, towards the lower limit of the stress range, no clear examples of type (a) were found (similarly, at the upper limit, no clear examples of type (b) were found). For this reason it is concluded that the appearance does not belie the reality, and that with diminishing stress there is a genuine change from wedge-shaped cracks based on a grain corner (type (a)) to separate cavities lying anywhere in a grain boundary (type (b)).

Excepting in Nimonic 80A, the type-(a) cracks form only if the applied stress is greater than about 5–8 tons/in.<sup>2</sup>. In Nimonic 80A they do not form below 15 tons/in.<sup>2</sup>, but, as mentioned earlier, comparison with Nimonic 90 shows that this is probably a result of the fast formation of type-(b) cavities in Nimonic 80A. That is to say, if the formation of type-(b) cavities could be suppressed, type-(a) cracks would presumably form in Nimonic 80A below 15 tons/in.<sup>2</sup>. Indeed, there is no proof that if the formation of type-(b) cavities were

suppressed in the other materials, type-(a) cracks would not form below 5 tons/in.<sup>2</sup>.

It is interesting to see whether this figure is consistent with Stroh's theory.<sup>5</sup> This was worked out for the stress concentration at the head of a slip band, but it applies also to that at the end of a sliding grain boundary, since the calculation is independent of the nature of the sliding interface. In this theory the criterion for a crack to form is that the elastic energy associated with the stress concentration is greater than the sum of the elastic and surface energies of the smallest stable crack that could form. It is found that a crack forms when:

$$\sigma^2 \geq \frac{12\gamma G}{\pi L}, \quad \dots \dots (1)$$

where  $\sigma$  is the applied shear stress,  $\gamma$  is the new surface energy per unit area of the surface of the crack formed,  $G$  is the shear modulus, and  $L$  is the length of the sliding interface. Stresses calculated from this equation for zinc and steel were found to agree with some measured data for these metals<sup>8,9</sup> to well within a factor of 2.

The present materials had grain-sizes ranging from 0.08 to 0.016 mm., so that  $L$  is about  $10^{-2}$  cm. With

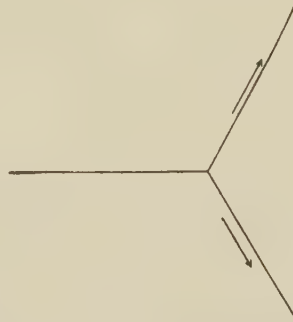


FIG. 11.—Symmetrical Arrangement Required at a Grain Corner if Equation (1) is to Hold.

$G = 8 \times 10^{11}$  dynes/cm.<sup>2</sup>,  $\sigma$  is  $2\frac{1}{2}$  tons/in.<sup>2</sup> (the maximum shear stress for a tensile stress of 5 tons/in.<sup>2</sup>) when  $\gamma$  is 450 ergs/cm.<sup>2</sup>. This is of the right order of magnitude, but on the low side; for the materials concerned, a value between 1000 and 2000 ergs/cm.<sup>2</sup> would be expected by comparison with known values for other metals.<sup>10</sup> Moreover, the estimate gives an upper limit, since it assumes the symmetrical arrangement depicted in Fig. 11, in which shear stresses cancel out. At grain corners where the arrangement is unsymmetrical, the stress concentration will be partly relieved by plastic flow and  $\gamma$  must be smaller than the value estimated if a crack is to form.

Fairly convincing evidence that the value of  $\gamma$  does influence the ease of cracking is that cracks sometimes stopped at twin boundaries, as in Fig. 7 (Plate LXXIV); it is hard to see any reason for this other than a change in  $\gamma$  due to a change in the grain-boundary free energy, which is known to depend on the orientation change across the boundary. In the present materials  $\gamma$  may be lower than it would be in a pure metal, since impurities should be capable of reducing  $\gamma$  substantially, as a detergent reduces the surface tension of water, and examples of this in solid metals are known.<sup>11,12</sup> Practical experience with creep-resistant alloys has shown that some

impurities are harmful. The occurrence of many more cracks than usual in bands of presumably irregular composition in G32 and Rex 337A has already been mentioned and probably presents an example of impurities making it easier for cracks to form. It may therefore be that if the content of certain impurities could be reduced still further, these materials would fracture less easily.

Once type-(a) cracks have formed, they can grow by the action of the stress and by the precipitation of vacancies, as has been suggested.<sup>1</sup> Precipitation of vacancies seems necessary to account for the width of the crack in Fig. 8, where it meets the twin boundary; otherwise sliding at the twin boundary would have to be assumed, although it never appears to have been observed. Presumably the ledge at the twin in Fig. 1 was produced because the crack developed in the way shown in Fig. 8 before spreading into the region where the twin meets the boundary.

Type-(b) cavities also need an artificial nucleus. This is discussed elsewhere,<sup>13</sup> the suggestion being that they nucleate at ledges in sliding boundaries. If it were possible for the ledges to be of only atomic dimensions, a very small applied stress should be able to nucleate cracks in this way. The nuclei could perhaps grow by a combination of sliding and slip until they were large enough to be stable in the prevailing vacancy concentration, but the properties of the particular metal would determine whether this is likely or not.

According to this, if type-(b) cavities can form, they should be able to form under all the test conditions investigated here. From the experimental results, however, it appears that at high stresses fracture occurs by the growth of cracks started at grain corners before many type-(b) cavities have enlarged to visible size.

An intriguing point is the variation in the number of cracks in the broken specimens. For example, there were hardly any in the Nimonic 80 specimens, but plenty in most of the other specimens. Moreover, the number

hardly varied with the test conditions in Rex 337A, but varied considerably and more or less systematically in Nimonic 90 and G32. In some specimens, therefore, an early crack spreads across the section before many cracks form elsewhere, whereas in others numerous cracks form before any one grows large enough to cause fracture. It is clear that the relative rates of formation and of growth of cracks must vary widely to bring about these results.

#### ACKNOWLEDGEMENTS

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# THE EFFECT OF HEAT-TREATMENT AND STRUCTURE <sup>1777</sup> ON THE CREEP AND STRESS-RUPTURE PROPERTIES OF NIMONIC 80A \*

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## SYNOPSIS

The influence of various stages of heat-treatment on the structure and the creep properties, at 750° C., of the nickel-chromium alloy hardened with titanium and aluminium, known as Nimonic 80A, has been studied. It is shown that three factors control the creep characteristics:

- (1) The time and temperature of solution-treatment largely determine the creep rate, temperature having the predominant effect.
- (2) Precipitation of chromium carbide at the grain boundaries largely determines the amount of creep extension which occurs before fracture.
- (3) The time and temperature of precipitation of the normal hardening phase,  $\text{Ni}_3(\text{Ti}, \text{Al})$ , affects, to a lesser degree, both creep rate and extension at fracture.

## I.—INTRODUCTION

THE research work which led to the development of Nimonic 80A, a titanium- and aluminium-hardened nickel-chromium alloy widely used for severely stressed components operating at high temperatures, such as gas-turbine blades, has been described by Pfeil, Allen, and Conway.<sup>1</sup> Typical compositions of the alloy are given in Table I. Under the conditions in which that work was carried out, it had been necessary to concentrate on immediately important practical aspects, associated with war-time requirements, rather than to study completely the details of structure which produce the best resistance to creep.

Subsequently the constitution of the alloys was more fully investigated, and the findings, associated with empirically determined effects of heat-treatment variables, indicated clearly that the optimum creep properties were not developed by a simple process of precipitation-hardening. The precipitating phase of the type  $\text{Ni}_3(\text{Ti}, \text{Al})$ , called  $\gamma'$  by Taylor and Floyd<sup>2</sup> in their investigation of the nickel-chromium-aluminium ternary system, is completely dissolved in the matrix at temperatures above about 875° C. and produces hardening of the alloy when precipitated by heating at lower temperatures. The creep and stress-rupture properties of the alloy at about 700° C. were, however, found to be optimum when solution-treatment was carried out at about 1080° C.; lower temperatures led to higher creep rates, and higher temperatures caused early rupture at small values of creep strain.

The investigation reported in the present paper was undertaken to study these effects more fully. The account of this work may conveniently be divided into two sections, the first describing preliminary experiments of a varied nature which led to an understanding of the phenomena influencing the properties of the alloy, and

the second describing a carefully controlled series of tests made to assess the effects of different heat-treatments on the creep properties.

## II.—PRELIMINARY EXPERIMENTS

Two simple observations on the effect of heat-treatment on creep had indicated that the development of good creep properties was not, in the case of Nimonic 80A, a simple precipitation-hardening mechanism: (i) in spite of almost uniform hardening after solution-treatment at various temperatures within the range 900°–1200° C., the creep properties reached a maximum when a solution temperature in the region of 1050°–1100° C. was used; and (ii) while solution-treatment at a temperature around 1200° C. gave poor creep properties in material subsequently aged in the normal manner at 700° C., the properties could be improved by giving a second "solution" treatment in the range 1050°–1100° C.

It was thought that effect (i) might be associated with incomplete solution of the hardening phase, which resulted in the formation of nuclei favourable to later precipitation, the optimum temperature being a consequence of the slow rate of solution of the precipitating phase. An alternative possibility was that a critical amount of residual cold work might be desirable, the optimum temperature in this case being determined by the rate of strain relief. Effect (ii) was thought to indicate that, whereas treatment at 1200° C. takes all constituents into solution, so that subsequent precipitation at about 700° C. is discontinuous, an intermediate treatment at 1050°–1100° C. might precipitate some phase which could serve to nucleate general or continuous precipitation of the major hardening phase.

It was considered that further assessment of these effects and their relative significance could be rapidly

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obtained by using hardness measurements to indicate the solution or precipitation of constituents and by microscopic observations to follow the character of the precipitation.

The material used for these experiments was hot-rolled bar from heat *A*, the composition of which is given in Table I.

TABLE I.—*Analyses of Alloys Used.*

Heat	Cr, %	Ti, %	Al, %	C, %	Fe, %	Si, %	Mn, %	Cu, %
A	20.00	2.29	1.26	0.02	0.31	0.38	0.18	0.04
B	20.65	2.47	1.20	0.17	0.51	0.79	0.27	...
C	19.20	2.44	1.09	0.04	0.41	0.59	0.08	0.05
D	20.67	2.47	1.23	0.01	0.28	0.58	0.36	...
E	19.07	2.33	0.99	0.07	0.42	0.62	0.09	0.10
F	19.90	2.33	1.20	0.08	0.63	0.53	0.11	0.04

The first series of tests was planned to show whether the solution process was relatively so slow that even if 1080° C., the normal temperature for this operation, was above the solubility limit, the phase would not be fully dissolved after 8 hours' treatment. The samples were first solution-treated at 1225° C. for 4 hr. (to remove any cold work), aged at 800° C. for 24 hr. (to produce heavy precipitation), and then solution-treated at 1080° C. for periods varying between  $\frac{1}{2}$  and 100 hr., and water-quenched. Hardness measurements were then made, and the two samples which had been subjected to the longest and the shortest solution times at 1080° C. were microscopically examined. All the samples were then aged for 16 hr. at 700° C. and their hardness was again tested. The hardness values are given in Table II, and the structures of the samples treated for the shortest and the longest periods, respectively, are shown in Figs. 1 and 2 (Plate LXXV).

TABLE II.—*Brinell Hardness Values after Various Solution-Treatment Times at 1080° C.*

Samples initially soaked at 1225° C. for 4 hr. and aged at 800° C. for 24 hr.

Solution-Treatment *	Average Hardness Number (2 mm./120 kg.)	
	Solution-Treated	Aged 16 hr. at 700° C.
$\frac{1}{2}$ hr. at 1080° C., W.Q.	168	277
2 hr. at 1080° C., W.Q.	169	285
8 hr. at 1080° C., W.Q.	165	283
50 hr. at 1080° C., W.Q.	168	285
100 hr. at 1080° C., W.Q.	159	...

\* W.Q. = Water-quenched.

The results given in Table II show no significant variation of hardness with time of solution-treatment at 1080° C., and it was therefore concluded that the rate of solution of precipitated material is relatively fast and that the normal time of treatment (8 hr. at 1080° C.) is adequate to ensure complete solution of the constituent, which is subsequently precipitated at 700° C., and which is responsible for the major hardening effect. Nevertheless, the structures shown in Figs. 1 and 2 indicate that some phase insoluble at 1080° C. is being concen-

trated at the grain boundaries during prolonged treatment at that temperature, whether or not it had been taken into solution by the treatment at 1225° C. It remained an open question whether this phase was being slowly precipitated at 1080° C., or whether it was merely agglomerating.

The object of the second series of tests was to determine the rate of relief of work-hardening during solution-treatment at 1080° C. A bar  $1\frac{1}{2}$  in. square was forged to approximately  $1 \times \frac{5}{8}$ -in. section and solution-treated for 4 hr. at 1225° C. and water-quenched. It was machined to a section  $1 \times 0.4$  in. and then cold-rolled to 0.25-in. thickness. A corresponding sample was machined to the same thickness immediately after being solution-treated in the same manner. Short lengths were cut from each bar and solution-treated at 1080° C. for periods varying from  $\frac{1}{2}$  to 100 hr., and their hardness was tested. The results are given in Table III. Microscopical examination showed that while all the cold-worked samples had a fine grain-size, with evidence of slight coarsening as the time of treatment increased, all the samples initially treated at 1225° C. without prior cold work had a large grain-size.

TABLE III.—*Rate of Relief of Work-Hardening.*

Solution-Treatment *	Average Hardness Number (2 mm./120 kg.)	
	Cold Worked 37½% Reduction	4 hr. at 1225° C., W.Q.
None	347	...
$\frac{1}{2}$ hr. at 1080° C., W.Q.	191	151
2 hr. at 1080° C., W.Q.	180	161
8 hr. at 1080° C., W.Q.	188	161
16 hr. at 1080° C., W.Q.	173	162
50 hr. at 1080° C., W.Q.	180	...
100 hr. at 1080° C., W.Q.	173	...

\* W.Q. = Water-quenched.

The figures in Table III indicate that cold work is relieved fairly rapidly at 1080° C.; the hardness value as cold-worked of 347 is reduced to 191 after a  $\frac{1}{2}$ -hr. treatment and to 180 after a 2-hr. treatment, but there is no further significant change up to 100 hr. The consistent difference between the cold-worked specimens and the material given the same heat-treatment without prior cold work is probably due to differences in grain-size.

Two final series of samples were prepared for microscopical observation of any variations in the character of the precipitation which might be produced by various cooling and ageing treatments after solution-treatments of 8 hr. at 1080° C. and 4 hr. at 1225° C., respectively.

After the treatment at 1080° C., samples were: (a) cooled in sand, (b) air-cooled, (c) hot-water-quenched, (d) hot-water-quenched, aged for 2 hr. at 800° C., and air-cooled, and (e) hot-water-quenched, aged for 2 hr. at 850° C., and air-cooled.

After the treatment at 1225° C., samples were: (a) air-cooled, (b) hot-water-quenched, (c) air-cooled, treated for 8 hr. at 1080° C., and hot-water-quenched.

All the samples were finally aged for 16 hr. at 700° C. before examination. The grain-size of all the samples solution-treated only at 1080° C. was mixed; the mean diameter of the grains was of the order of 0.10 mm., with a preponderance about 0.02 mm. in mean diameter. All



the samples heated to 1225° C. had a more uniform, coarser grain-size, the mean diameter being 0.25 mm. The character of the precipitation showed little change with variation in rate of cooling from the solution temperature, although with the faster rates of cooling, dark-etching crescent-shaped areas at the boundaries (believed to be indicative of discontinuous precipitation of the  $\text{Ni}_3(\text{Ti}, \text{Al})$  phase) tended to be more plentiful. Change in the solution-treatment temperature resulted in but little difference in the appearance of these crescents. Indications of general precipitation of a phase throughout the grains were obtained only in the two samples which were solution-treated at 1080° C. and aged at 800° or 850° C.

Light-etching particles were observed in the grain boundaries, similar to those shown in Fig. 1 (Plate LXXV); these were particularly numerous in the samples treated first at 1225° and then at 1080° C. They were observed also, although in lesser amount, in the samples aged at 850° C. after solution-treatment at 1080° C., but they were not visible in those treated only at 1225° C.

The microscopic examination did not confirm the hypothesis that discontinuous precipitation is obtained by treatments which give poor creep properties, but it provided valuable new information by revealing the presence of the white grain-boundary constituent resulting from heating at 1080° C. It seems possible that the presence of this constituent, either by its direct effect or by its influence on the manner of deposition of the main precipitable constituent, favours good creep properties, since it is definitely absent after solution-treatment at 1250° C. (which is associated with poor creep properties), but appears on subsequent heating at 1080° C. (a treatment which was known to improve the creep properties).

In order to determine the nature of this grain-boundary phase, samples of three heats (*B*, *C*, and *D*) of the alloy were studied by microradiography. The compositions of the heats are given in Table I. They were selected on the basis of varying carbon content. The phase was precipitated at the grain boundaries by solution-treatment for 3 hr. at 1250° C., followed by cooling direct to 1050° C. and holding at that temperature for 16 hr. Microscopic examination showed heavy precipitation of the phase in heat *B*, appreciably less in heat *C*, and only traces in heat *D*; in view of the variation in relation to the carbon content, this suggested that the phase was a carbide. Microradiographs were prepared from each sample, by the technique described by Betteridge and Sharpe,<sup>3</sup> using the characteristic radiations of chromium and of iron, which enabled nickel, chromium, and titanium to be differentiated by their linear coefficients of absorption. The radiographs for heat *B* are illustrated in Figs. 3 (*a*) and (*b*) (Plate LXXV). The change in contrast relative to the matrix of the alloy is sufficient to indicate that the grain-boundary phase is chromium-rich, since no other element except vanadium could produce the same effect, and this element was not present in the alloy. The particles of titanium cyano-nitride, which are always present in Nimonic alloys as orange-coloured cuboids, appear as white spots in the radiograph taken with chromium radiation (Fig. 3 (*a*)), but are invisible in Fig. 3 (*b*), taken with iron radiation. In both radiographs a certain amount of chromium impoverishment is visible around the grain-boundary phase.

Formation of a chromium carbide in the presence of more than 2% titanium in solid solution was unexpected, since titanium is usually regarded as having a higher affinity for carbon than has chromium. Confirmatory experiments were therefore carried out, by electrolytic or chemical extraction of the phase and examination by X-ray analysis. Extraction was effected by various techniques: (i) Anodic solution in 5% aqueous hydrochloric acid, at about 0.05 amp./cm<sup>2</sup>; (ii) as (i), but using 5% alcoholic hydrochloric acid; (iii) solution in acidified cuprous ammonium chloride; and (iv) solution in bromine-ester mixtures.

The extracts were washed, centrifuged, and dried, and X-ray diffraction patterns were prepared, using manganese  $K\alpha$  radiation. The phases present were identified by reference to known structures. The exact composition of each phase was not determined by chemical analysis, since the X-ray examination showed that a clean separation had not been achieved. It could be seen, for example, that faint lines, attributable to the nickel-chromium matrix, were also present. These did not interfere, however, with the qualitative identification of the principal phases.

Samples from a number of different batches of Nimonic 80A were examined, in two conditions of heat-treatment: (i) solution-treated for 3 hr. at 1250° C. and water-quenched, and (ii) solution-treated for 3 hr. at 1250° C., furnace-cooled to 1000° C., and held for 16 hr. In condition (i), all the heats examined (carbon varying between 0.01 and 0.10%) showed only the presence of compounds with the same cubic structure as  $\text{TiC}$  or  $\text{TiN}$ , though with intermediate lattice parameters and presumably containing both carbon and nitrogen. These titanium cyano-nitride inclusions are known, from metallographic studies, to remain unchanged by thermal treatments and to take no part in the hardening process. After treatment (ii), the samples with carbon contents above about 0.02% contained, in addition to the above titanium compounds, the chromium carbide  $\text{Cr}_7\text{C}_3$ . There was, therefore, no reasonable doubt that the grain-boundary phase illustrated in Fig. 2 was, in fact, this compound.

### III.—GENERAL SERIES OF INVESTIGATIONS.

Since the results described in Section II had indicated that the precipitation of chromium carbide represents an important structural change occurring at temperatures in the region of the normal solution-treatment temperature, a systematic investigation of the effects of such precipitation on the creep and rupture properties of the alloy was undertaken. The study was carried out in three stages: first, determination of the effect of treatments at temperatures between 1150° and 700° C. after solution-treatment at 1250° C.; second, determination of the effect of various treatments in the range 1000°–700° C. after precipitation of chromium carbide to an approximately optimum degree, as determined in the first stage; and finally, determination of the effect of variation in the solution-treatment temperature when followed by given precipitation treatments.

In all this work the creep-testing was carried out in one of two types of machine: (1) the T 46 radial-type creep unit, manufactured by Samuel Denison and Son, Ltd., of Leeds, in which twelve test locations surround

the central pillar of the unit and in which creep strain is measured with dial-gauge extensometers attached to the shackles holding the test bar; or (2) the single-unit machine described by Weaver,<sup>4</sup> in which creep strain is measured by a dial-gauge operating on the loading lever. In neither case are the strain measurements of high accuracy, but the results are found to be suitable for this class of work, in which rupture time is considered a more important criterion than creep strain. In both machines the same type of test-bar was used, having a parallel gauge-length 0.252 in. in dia. and  $2\frac{1}{4}$  in. long, with  $\frac{1}{2}$ -in. Whitworth screwed ends. The material used for the tests was  $\frac{5}{8}$ -in.-dia. hot-rolled bar, which was heat-treated by the selected procedures before the test-bars were machined.

#### 1. VARIATION OF INTERMEDIATE TREATMENT

For this stage of the investigation, the test-bars were initially solution-treated for 3 hr. at 1250° C., a temperature which had been shown by preliminary work to be

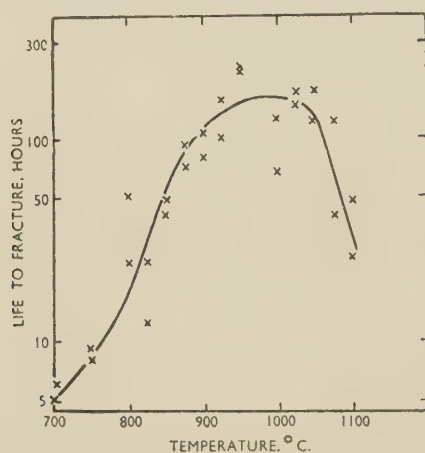


Fig. 6.—Relationship between Life-to-Fracture at 17 tons/in.<sup>2</sup> and 750° C. and the Temperature of Intermediate Treatment.

sufficient to take all the chromium carbide into solution. The bars were then transferred, without intermediate cooling, to furnaces at various lower temperatures, where they were held for 24 hr., after which time they were water-quenched and finally aged for 16 hr. at 700° C. Small samples were taken from the bars for metallographic study, and creep-test specimens were machined from the remainder. For this work heat *E* was used. All the creep tests were made at 750° C. under a stress of 17 tons/in.<sup>2</sup>, and the results obtained are recorded in Table IV. In Fig. 6 life-to-fracture, on a logarithmic scale, is plotted against the temperature of the intermediate treatment.

Ageing at 700° C., after solution-treatment, resulted in very short lives, but the lives increased progressively as the temperature of the second treatment was raised, until a maximum was reached for specimens treated at temperatures in the range 950°–1050° C.

The changes in microstructure observed in this series of specimens can be described by means of a few illustrations. In material treated only at 700° C., after solution-treatment, an acicular structure, believed to be typical of carbide precipitation at low temperatures,

appeared, whilst the grain boundaries were fine, dark-etching, and contained no resolvable constituents. Little change occurred with the introduction of the intermediate treatment at 750° C. (Fig. 4 (a), Plate LXXVI). As the intermediate temperature was raised, general

TABLE IV.—Variation of Creep Properties (at 17 tons/in.<sup>2</sup> and 750° C.) with Temperature of Intermediate Treatment.

Heat-treatment: Solution-treated for 3 hr. at 1250° C., transferred to intermediate temperatures given below, and held for 24 hr.; water-quenched; aged for 16 hr. at 700° C.

Intermediate Treatment Temperature, °C.	Minimum Creep Rate, %/hr.	Time to Onset of Tertiary Creep, hr.	Time to Fracture, hr.	Elongation, %
700	...	...	6 5	1.9 0.6
750	...	...	9 8	0.6 0.5
800	0.0028 ...	...	50 24	0.4 0.7
825	...	...	12 24	0.9 1.0
850	0.0146 0.0067	24 27	40 48	1.2 1.2
875	0.0052 0.0046	30 32	70 91	1.4 1.9
900	0.0023 0.0035	51 28	105 80	3.3 2.8
925	0.0052 0.0015	46 30	99 151	4.8 6.9
950	0.0030 0.0026	90 102	227 216	2.3 2.1
1000	0.0026 0.0041	32 28	122 63	2.6 1.3
1025	0.0015 0.0019	57 58	164 143	3.6 3.6
1050	0.0012 0.0020	136 93	170 121	0.4 2.3
1075	0.0058 0.0018	24 79	40 120	0.7 1.2
1100	0.0043 0.0032	... ...	25 47	0.5 0.6

precipitation of the  $\text{Ni}_3(\text{Ti}, \text{Al})$  phase appeared in the grains. At temperatures approaching the upper limit of occurrence of the  $\text{Ni}_3(\text{Ti}, \text{Al})$  phase, i.e. 825°–850° C., another phase could be resolved, in the grain boundaries, although its particles were not large enough to be positively identified. When the solubility limit of the main  $\text{Ni}_3(\text{Ti}, \text{Al})$  phase was exceeded, the grain boundary contained slightly larger particles (which could then be identified as chromium carbide), whilst other particles of similar size, shape, and appearance could be detected within the grains themselves. Further rise of temperature, up to approximately 1000° C., caused the amount of carbide at grain boundaries to increase and the amount in the grains to decrease. This condition is illustrated in Fig. 4 (b) (Plate LXXVI), which relates to an inter-



mediate temperature of 950° C. Over the temperature range 1000°–1150° C., the individual particles became larger, presumably as a result of coalescence, and tended to be confined to the grain boundaries; after treatment at the highest temperatures, it was common to find that large globules of carbide appeared only on parts of a boundary, the other parts being fine, dark-etching, and free of resolvable particles (Fig. 4 (c), Plate LXXVI), which illustrates the condition after an intermediate treatment at 1075° C. In none of the specimens treated at the higher range of intermediate treatments were the boundaries quite free of any precipitated carbide; presumably the highest temperature used, although approaching that of complete solution of chromium carbide, did not exceed it. The hardness values recorded on these samples before and after the final ageing treatment at 700° C. are also of interest (Fig. 7). The highest final

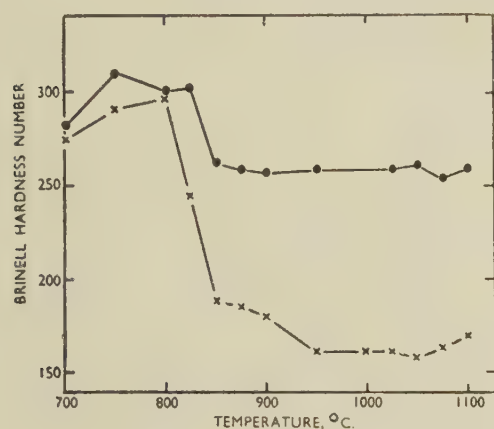


FIG. 7.—Relationship between Brinell Hardness and Temperature of Intermediate Treatment: × before ageing for 16 hr. at 700° C.; ● after ageing for 16 hr. at 700° C.

hardnesses were obtained only when the second treatment temperature was in the range 700°–825° C., which resulted in only slight precipitation of chromium carbide at the grain boundaries. Presumably, if the carbide is generally and finely distributed, it adds to the hardening produced by precipitation of the  $\gamma'$  phase, but when deposited at the grain boundaries it is ineffective in this respect.

Consideration of the stress-rupture results in the light of the corresponding structures and hardness values indicates that the best life-to-fracture is obtained after treatments which produce a fairly uniformly distributed chain of chromium-carbide particles along the grain boundaries. The hardness appears to have little influence, however, since a wide range of lives was recorded as the second-treatment temperature was varied between 850° and 1100° C., although the hardness was almost constant for all these samples.

## 2. EFFECT OF AGEING TREATMENT AFTER OPTIMUM PRECIPITATION OF CHROMIUM CARBIDE

For this series of tests, a constant and nearly optimum condition of precipitation of the chromium carbide was selected on the basis of the treatments investigated in the previous series. The test-bars were again from heat E,

and the lengths of  $\frac{5}{8}$ -in.-dia. bar were initially heated to 1250° C. for 3 hr. and furnace-cooled to 1000° C., at which temperature they were held for 16 hr. At this stage the specimens had a satisfactory distribution of chromium carbide at the grain boundaries. The bars were then transferred to other furnaces at various temperatures in the range 700°–1000° C. and held at the respective temperatures for 16 hr. These treatments produced various amounts and varying distributions of the  $\gamma'$  precipitate, which is responsible for the major part of the hardening. The bars were then water-quenched and finally aged for 16 hr. at 700° C., so that little further change in hardness should have taken place during subsequent creep testing at 750° C. Small samples for hardness determinations and microscopic examination were taken from the bars at various stages during the treatments.

The creep-test results obtained on this series of bars are recorded in Table V, from which it will be noted that the variations in life lay within much narrower limits than those observed in the first series of tests, although a minimum life associated with a maximum elongation is given by treatment at 875° C., i.e. just about the temperature for complete solubility of the  $\gamma'$  phase in this particular cast.

TABLE V.—Variation of Creep Properties (at 17 tons/in.<sup>2</sup> and 750° C.) with Temperature of Ageing Treatment.

Heat-treatment: solution-treated for 3 hr. at 1250° C., cooled directly to 1000° C. and held at that temperature for 16 hr.; transferred directly to preliminary ageing temperatures given below; held for 16 hr.; water-quenched; aged for 16 hr. at 700° C.

Treatment Temperature, °C.	Minimum Creep Rate, %/hr.	Time to Onset of Tertiary Creep, hr.	Time to Fracture, hr.	Elongation, %
700	0.0018 0.0022	74 62	136 182	4.1 3.7
750	0.0008 0.0015	36 38	102 119	0.9 2.1
800	0.0031 0.0054	27 69	144 121	N.D.* 4.8
825	0.0136 0.0060	24 26	77 97	6.03 4.7
850	0.0116 0.0055	26 28	76 121	8.9 4.5
875	0.0116	24	64	>10
900	0.0036 0.0005	39 60	101 184	5.6 4.9
925	0.0023 0.0047	55 36	79 55	0.9 4.1
1000	0.0018 0.0020	72 50	197 131	5.2 2.1

\* N.D. = Not determined.

Fig. 5 (Plate LXXVI) shows typical microstructures for samples treated at 800°, 850°, and 900° C. From these it is apparent that the changing amount and distribution of the  $\gamma'$  phase have no visible effect on the grain-boundary carbide precipitate. Furthermore, as the majority of the carbide was precipitated at the boundaries by the

initial treatments, the acicular structure previously observed as associated with low-temperature treatments did not appear. The hardness values recorded for this series of tests before and after the final treatment at 700° C. are plotted in Fig. 8. The general trend of hardness with temperature of initial precipitation-treatment is similar to that found in the earlier series, illustrated in Fig. 7, although in the present series the maximum hardness attained is lower. This is due to a

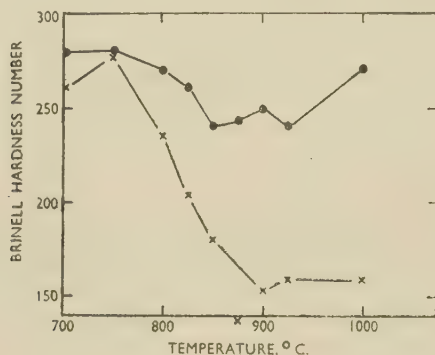


FIG. 8.—Relationship between Brinell Hardness and Temperature of Ageing: × before ageing for 16 hr. at 700° C.; ● after ageing for 16 hr. at 700° C.

substantial proportion of the carbide having been precipitated at the grain boundaries and thus being unable to contribute to the general hardness of the grains.

### 3. EFFECT OF SOLUTION-TREATMENT TEMPERATURE

The tests already described had established that correct grain-boundary precipitation of carbide is a most important factor in obtaining the best creep properties, and that precipitation of the  $\gamma'$  phase is of less importance. Thus, by maintaining constant conditions of precipitation of these two phases, it was now possible to study the effect, on creep properties, of variation in the solution-treatment temperature. For this purpose, samples of heat *F* were used. Bars,  $\frac{5}{8}$  in. in dia., were submitted to the following treatments: the hot-rolled bars were solution-treated for 4 hr. at temperatures varying in steps of 50° C. over the range 1000°–1250° C.; they were then furnace-cooled to 1000° C. and held at that temperature for 16 hr. in order to obtain as constant a degree of carbide precipitation as possible. They were then air-cooled and aged for 16 hr. at 700° C. The creep-test results obtained are recorded in Table VI, in which the grain-sizes, determined metallographically by the intercept method upon the actual creep-test bars, are also included. From these results it is apparent that some correlation between creep life and grain-size exists, although it is by no means certain that life is directly dependent on grain-size. The results indicate that the longer lives obtained after solution-treatment at 1150° C. and above are associated with a markedly reduced minimum creep rate. Overall elongation-to-fracture also falls to a lower level as the life increases.

As was indicated in the Introduction, normal practice is to use a solution-treatment of 8 hr. at 1080° C., followed by air-cooling and ageing for 16 hr. at 700° C. By this method a suitable compromise between the conflicting

requirements of reasonably fine grain-size and high creep-resistance is obtained by means of a relatively simple heat-treatment procedure. A final series of tests on heat *F* was carried out to illustrate the nature of this

TABLE VI.—*Variation of Creep Properties (at 17 tons/in.<sup>2</sup> and 750° C.) with Solution-Treatment Temperature.*

Heat-treatment: solution-treated at given temperature for 4 hr., cooled directly to 1000° C. and held for 16 hr.; air-cooled; aged for 16 hr. at 700° C.

Solution-Treatment Temperature, °C.	Creep Properties				Brinell Hardness No.		Mean Grain Dia., mm.
	Minimum Creep Rate, %/hr.	Time to Onset of Tertiary Creep, hr.	Life to Fracture, hr.	Elongation, %	Before Test	After Test	
1000	0.0069 0.0050	60 50	131 130	4.0 5.2	315	342	0.024
1050	0.0056 0.0033	55 40	110 156	2.7 4.5	316	344	0.027
1100	0.0031 0.0084	44 98	173 150	4.0 3.3	306	338	0.028
1150	... 0.0005	... 295	390 407	1.2 1.4	294	313	0.226
1200	0.0002 0.0004	225 344	430 623	1.4 2.9	274	305	0.192
1250	0.0009 0.0004	306 250	405 452	1.3 1.9	274	297	0.221

TABLE VII.—*Variation of Creep Properties (at 17 tons/in.<sup>2</sup> and 750° C.) with Solution-Treatment Temperature.*

Heat-treatment: solution-treated at given temperature for 8 hr., air-cooled, and aged for 16 hr. at 700° C.

Solution-Treatment Temperature, °C.	Creep Properties				Brinell Hardness No.		Mean Grain Dia., mm.
	Minimum Creep Rate, %/hr.	Time to Onset of Tertiary Creep, hr.	Time to Fracture, hr.	Elongation, %	Before Test	After Test	
1000	... 0.0120	... 28	77 72	5.4 3.4	322	336	0.018
1050	0.0061 0.0056	49 38	147 124	5.5 2.8	322	338	0.027
1080	0.0036 0.0031	34 24	139 140	3.1 2.3	308	345	0.028
1100	0.0048 0.0037	40 32	128 103	2.5 1.3	314	351	0.029
1150	0.0011 0.0006	... ...	49 73	0.6 0.6	283	321	0.147
1200	...	...	5	0.8	277	338	0.229
1250	... ...	... ...	8 9	1.2 0.5	283	343	0.247

compromise. Lengths of  $\frac{5}{8}$ -in.-dia. hot-rolled bar were solution-treated for 8 hr. at temperatures within the range 1000°–1250° C., air-cooled, and finally aged for 16 hr. at 700° C. The bars were tested in duplicate at a



stress of 17 tons/in.<sup>2</sup> at 750° C.; the results are given in Table VII. These data, and also those obtained from the previous series of experiments, are summarized in Fig. 9, where the mean life-to-fracture of each pair of bars is plotted against solution-treatment temperature. In both instances the short life obtained after treatment at the lowest temperatures was associated with high creep rates and high total elongations. When the intermediate treatment at 1000° C. was omitted, maximum life was obtained with a solution-treatment temperature in the range 1050°–1080° C., and the shorter life at higher solution-treatment temperatures was associated with lower creep rates and lower total-elongation values. On the other hand, the addition of an intermediate treatment at 1000° C., to cause a carbide precipitate, prevented

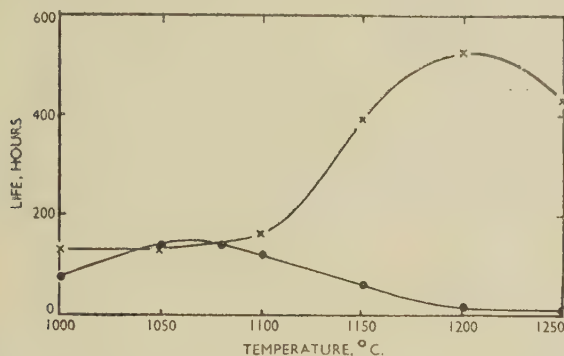


FIG. 9.—Influence of Solution-Treatment Temperature on Life at 17 tons/in.<sup>2</sup> and 750° C. × Solution-treated for 4 hr., cooled to 1000° C. and held for 16 hr., air-cooled, and aged for 16 hr. at 700° C.; ● solution-treated for 8 hr., air-cooled, and aged for 16 hr. at 700° C.

early fracture at low extension and led to an appreciable increase in creep life as the solution-treatment temperature was raised.

#### IV.—DISCUSSION OF RESULTS

This investigation has shown that the influence of heat-treatment and structure on the creep properties of Nimonic 80A at 750° C. is characterized by three main features.

Complete solution of essential phases is effected only at temperatures above about 1150° C., and when this is achieved marked grain growth occurs. Solution-treatments of this complete type lead to low creep rates, independent of the subsequent stages of heat-treatment, although it is not established whether the low creep rate is a direct consequence of the large grain-size, or whether these two properties are separately dependent upon a more fundamental variable, such as the perfection of the crystal lattice. It has been shown by Betteridge<sup>5</sup> that the creep-resistance of pure aluminium at 200° C. increases progressively with increase of annealing temperature without any structural changes, and it seems probable that the same mechanism might operate in a complex alloy, particularly at temperatures at which the alloy has a single-phase structure. From this viewpoint the solution-treatment can be regarded as having two

functions: to dissolve the phases to be precipitated later and to anneal the matrix. The latter process is thought to be the important factor in promoting high creep-resistance.

The manner of precipitation of chromium carbide has an important influence on the amount of creep extension which occurs before fracture, and by maintaining the alloy at a temperature in the region of 1000°–1050° C., a favourable distribution of carbide at the grain boundaries is obtained. If such a condition is not obtained, fracture occurs at a relatively small extension, and in spite of a low creep rate, the life can be very short. It seems likely that the effect of the precipitation of carbide is to produce, around the boundaries, zones which are impoverished in chromium and, therefore, reduced in strength. These zones permit the relaxation of stresses which, in creep, are known to concentrate at the boundaries, particularly at triple points, and which otherwise would lead to the formation of cracks. The early cracking, at low extension, of material not showing satisfactory carbide precipitation supports this view.

Variation in the temperature of precipitation of the  $\gamma'$  phase affects, to a small degree, both the creep rate and the extension at which fracture occurs, the lowest creep rate and the longest life being obtained after precipitation-treatment at a temperature no higher than that at which the creep test is made. When precipitation is initially carried out at a temperature only a little below the solubility temperature, the creep rate is increased and the life is reduced, with an increase in the total creep extension before fracture. Two factors which make it difficult unequivocally to isolate the effect of  $\gamma'$  precipitation are that, in spite of previous precipitation of chromium carbide at the grain boundaries, further precipitation of this phase may occur at lower temperatures and be confused with precipitation of  $\gamma'$ ; and that precipitation of  $\gamma'$  during the course of the creep test at 750° C. may mask to a considerable extent the effect of earlier precipitation.

The two-stage treatment normally used provides a reasonable compromise in properties. The temperature of solution-treatment is high enough to ensure a reasonably low creep rate, and is suitable also for the deposition, at the grain boundaries, of carbide taken into solution by earlier heating for hot working. Precipitation at 700° C. alone leads to a low creep rate and a long life, but some sacrifice in these properties by precipitation-treatment at higher temperatures will enable increased creep extension before fracture to be obtained.

#### ACKNOWLEDGEMENTS

The authors are indebted to The Mond Nickel Co., Ltd., for permission to publish this work.

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# 1778 INTERCRYSTALLINE CRACKING IN CREEP OF SOME ALUMINIUM ALLOYS\*

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## SYNOPSIS

The paper describes a systematic study of the occurrence of intercrystalline cracking during creep in two high-purity-base aluminium alloys containing 1.28 wt.-% manganese and 5.15 wt.-% magnesium, respectively. The constant-strain-rate method of deformation was employed.

The mode of fracture was examined over wide ranges of temperature and strain rate, and a relationship was obtained which represented the onset of intercrystalline cracking in the aluminium-manganese alloy. This relationship suggests that the mechanism of intercrystalline cracking is controlled by a rate process. Constant-load creep tests were performed to relate the state of development of cracks to the various stages of the conventional creep curve, and the form of intercrystalline cracks was studied by metallographic and X-ray methods. Intercrystalline fracture was observed in the aluminium-magnesium alloy in a central range of strain rate, but fractures outside this range appeared to be ductile. Metallographic examination showed that the relative extents of grain-boundary sliding and migration appear to control the development of cracks at grain boundaries during creep.

A general theory of intercrystalline cracking is proposed which employs a physical model based on the experimental observations.

## I.—INTRODUCTION

TERTIARY creep and fracture have received relatively little attention compared with the structural changes occurring during the primary and secondary stages of creep. Examples of intercrystalline cracking and fracture in various materials during creep have been reported in the literature, and recent papers reveal a tendency to study fracture for its own sake.

In an investigation of the behaviour of steels in creep, Dickenson<sup>1</sup> observed intercrystalline fracture in a specimen of cast nickel-chromium-iron alloy, and ascribed it to the weakening effect of particles of spheroidized carbide at the grain boundaries. Tapsell<sup>2</sup> found that certain nickel-copper, nickel-chromium, and nickel-chromium-iron alloys, subjected to prolonged loading, failed in an intercrystalline manner; there was little deformation of the grains, and cracks formed at those grain boundaries which were transverse to the direction of applied stress.

The researches of Hanson and Wheeler<sup>3</sup> revealed the intercrystalline nature of some creep fractures in polycrystalline aggregates and bicrystals of commercially pure aluminium. They showed that although cracks first became visible near the end of the secondary stage of creep, there had been a slow but definite fall in density before this, and they suggested that cracks were beginning to form much earlier in the secondary stage.

Intercrystalline cracking in creep was reported in mild steel and Armco iron<sup>4</sup> and in molybdenum and molybdenum-vanadium steels.<sup>5</sup> It was also reported in some

high-purity aluminium-iron alloys. A series of constant-load creep tests on high-purity aluminium-magnesium alloys by Mullendore and Grant<sup>6</sup> show that under certain conditions intercrystalline cracks form in these alloys. Intercrystalline cracking was reported in a copper-nickel-silicon alloy by Jenkins and his co-workers,<sup>7</sup> who found separate, rounded intercrystalline cavities near fractures that occurred with low reduction of area.

In a recent paper,<sup>8</sup> Carreker and Hibbard have confirmed the existence of a "transition temperature" between the transgranular and intergranular modes of fracture in high-purity copper, and have examined its variation with grain-size. The influence of strain rate was not studied.

Greenwood, Miller, and Suiter<sup>9</sup> found intergranular holes in copper,  $\alpha$ -brass, and magnesium during tests at constant strain rate and elevated temperatures. For each material the incidence of intercrystalline cracking was investigated at three widely differing strain rates over a range of temperature. It was found to be strongly dependent on these two variables and was associated with a loss of ductility.

With the exception of the last-mentioned work, it appears that no systematic investigation of the influence of strain rate on the mode of creep fracture has been carried out. The present investigation was designed to explore the relationship—if one exists—between temperature, strain rate, and the incidence of intercrystalline cracking. This might then form a quantitative basis for a physical model of the mechanism of intercrystalline cracking.

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## II.—EXPERIMENTAL

## 1. MATERIAL

The materials employed were two high-purity-base aluminium alloys containing 1.28% manganese and 5.15% magnesium, respectively. The aluminium-manganese alloy had a two-phase structure at all temperatures up to 620° C., the second phase being based on the intermetallic compound  $MnAl_6$ . The aluminium-magnesium alloy was a homogeneous solid solution above 270° C. Below this temperature, alloys in equilibrium contain a second phase having a hexagonal structure based on the composition aluminium 64, magnesium 36 wt.-%. The materials, together with the analyses given in Table I, were supplied by The British Aluminium Co., Ltd.

TABLE I.—Composition of Alloys and Mechanical Properties.

Alloy	No.	Si, %	Fe, %	Cu, %	Mn, %	Mg, %	U.T.S., tons/ in. <sup>2</sup>	Elong. % on 2 in.
Al-1½% Mn *	1	0.0035	0.0015	0.0010	1.28	...	6.45	49
Al-5% Mg *	4	0.0025	0.0020	0.0005	...	5.15	15.2	39

\* Special-purity base.

The materials had been extruded into  $\frac{3}{8}$ -in.-dia. rod. Short lengths of rod were cross-rolled into flat blanks from which specimens with gauge-sections measuring  $2 \times \frac{3}{8} \times \frac{1}{8}$  in. or  $1 \times \frac{1}{4} \times \frac{1}{8}$  in. were cut. These were mechanically polished on two flat faces and annealed for 24 hr. at 450° C. to permit recrystallization, followed by 24 hr. at the temperature at which they were to be tested. Specimens were given a final electropolish in a bath containing 10% perchloric acid in ethyl alcohol.

## 2. APPARATUS

Tests at constant strain rate were performed in a modified Hounsfield tensometer. A small furnace with a steel tube and both main and auxiliary windings was mounted on the slide-bars. Specimens were inserted, raised to test temperature, and held there for 24 hr. to achieve thermal equilibrium. Specimen temperature was controlled to within  $\pm 2^\circ$  C. by means of a thermocouple attached to the shoulder near the gauge-section. Temperature distribution along the specimen was made uniform by adjustment of the current through the auxiliary furnace windings. Specimens were deformed to fracture at predetermined rates by a constant-speed electric motor geared to the tensometer drive spindle.

Creep tests at constant load were performed in a modified Buckton single-lever tensile-test machine. The furnace, loading shackles, and extensometer were based on designs prepared by the British Non-Ferrous Metals Research Association adapted to conform with the size limits imposed by the Buckton machine. Temperature control was effected by utilizing the differential thermal expansion of the Inconel furnace tube and an Invar rod supported outside the furnace. This gave a control band of width  $\pm 0.1^\circ$  C., with a maximum drift of  $1^\circ$  C. in 100 hr. Extension of the specimen under test was measured by means of a pair of micrometer heads, to an accuracy of  $\pm 0.0005$  in.

## 3. RESEARCH PROGRAMME

Preliminary experiments showed that intercrystalline cracking occurred in specimens of the aluminium-manganese alloy deformed at constant strain rate to 10% elongation in 100 hr. at 300° C. (Fig. 7, Plate LXXXVII). Specimens of the aluminium-magnesium alloy deformed to the same extent under the same conditions showed no intercrystalline cracks.

The programme of investigations was divided into three main parts:

## Part 1

A series of tests was undertaken to determine, at selected temperatures, the strain rate at which intercrystalline fracture in the aluminium-manganese alloy is superseded by ductile fracture. At each test temperature, a series of specimens was deformed to fracture, each at a different strain rate. The values of strain rate employed increased in geometrical progression with ratio two. This was continued until the reduction of area at fracture had increased to a maximum and remained at an approximately constant value. Such test series were performed at temperature intervals of 100° C. in the range 200°–500° C. to evaluate the form of temperature-dependence of the transition from intercrystalline to transcrystalline fracture. Specimens with a 1-in. gauge-length were employed in order to achieve more easily a uniform temperature distribution along the gauge-length at higher test temperatures.

Reduction of area was adopted as the criterion of fracture type, since it was considered that the area of fracture was a sensitive guide to the ease with which an intercrystalline crack may propagate through a specimen, and to the state of crack development in a specimen at fracture. The transition from intercrystalline to transcrystalline fracture is not sharp, so the "transition point" was arbitrarily defined as the point at which reduction of area reached a maximum with increasing strain rate. Deformation at constant strain rate was employed because it was found that this method of testing made for easier interpretation of fractures. Specimens were taken to fracture at a constant strain rate and under a diminishing load, thereby avoiding the increasing creep rate and increasing stress which arises in tertiary creep at constant load.

The form of this part of the programme was such that the results might help to discriminate between the "stress-concentration" and "vacancy-migration" hypotheses for intercrystalline cracking in creep.

## Part 2

This took the form of a more detailed study of the development of cracks in polycrystalline specimens of the aluminium-manganese alloy. The formation of intercrystalline cracks in creep is of great importance, since it causes premature failure of specimens at low values of elongation. It was considered that valuable information could be obtained from a study of the time at which cracks first appeared and the stage of development at which they could propagate easily through the specimen.

Series of tests were performed both at constant load and at constant strain rate to determine whether similar effects were obtained in the two cases. Specimens were

deformed to various creep elongations and then fractured at a rapid rate at room temperature. Values for reduction of area and elongation to fracture were plotted against creep elongation as a guide to the influence of cracks at various stages of development on the ductility of specimens. This information was supplemented by the microscopic examination of unbroken specimens.

### Part 3

A series of tests was carried out in order to explore the fracture behaviour of the aluminium-magnesium alloy over a wide range of strain rate at a few selected temperatures.

The results of preliminary experiments on this alloy did not agree with work published later,<sup>6</sup> which suggested that intercrystalline cracking occurred in an alloy of this composition and became more prevalent at a given temperature as the strain rate was increased.

The grain-sizes of specimens employed in this series were represented by mean linear intercepts in the range 0.149–0.180 mm./grain, with a mean value of 0.163 mm./grain.

## 4. RESULTS

### Part 1

The results are shown graphically in Fig. 1, where reduction of area at fracture is plotted against the logarithm of strain rate. The plotted points lie on curves which represent increasing reduction of area with increasing strain rate, and denote a greater participation of necking and transcrystalline fracture in the fracture process. The curves reach a maximum reduction of area near 90%; at strain rates beyond this point, at any given temperature, the fractures change little in dimensions or appearance.

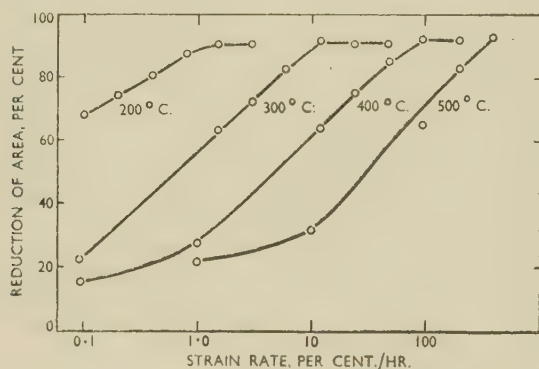


FIG. 1.—Reduction of Area Plotted Against Logarithm of Strain Rate for Specimens of the Aluminium–1½% Manganese Alloy.

The spacing of the curves in Fig. 1 resembles that which might be expected if temperature and transition strain rate were related through an exponential function representing a rate process. If such a relationship did exist, it could prove a valuable guide to the nature of the controlling process in the mechanism of creep fracture. In order to investigate the nature of the relationship, the values of strain rate at selected values of reduction of area were plotted on a logarithmic scale against the reciprocal of absolute temperature. This procedure implies that the rates of the activated process (if one

exists) at a given reduction of area at different temperatures can be represented by the corresponding values of strain rate.

The resulting curves are shown in Fig. 2. It is important to remember that the exact positions of the

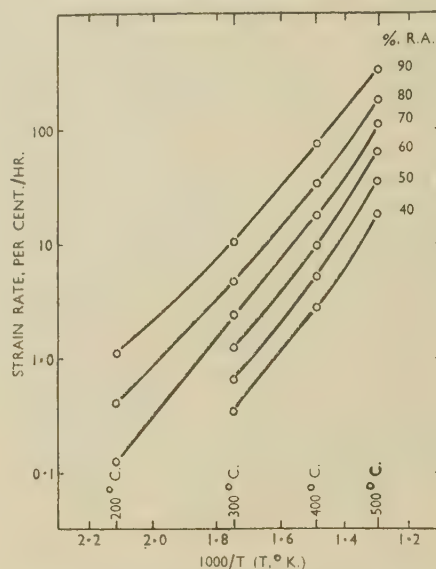


FIG. 2.—Logarithm of Strain Rate Plotted Against the Inverse of Absolute Temperature at Selected Values of Reduction of Area. Data derived from Fig. 1.

plotted points depend to some extent on the way in which the curves are drawn in Fig. 1. However, the shape of the curves in Fig. 2 is such that they may be claimed to represent the existence of some rate-controlling process in the mechanism of fracture. The values of the activation energy derived from this graph range from 15.2 to 17.9 k.cal./mole. The change of slope of the curves in Fig. 1 at about 90% reduction in area was found to coincide with the appearance of grain-boundary sliding at each temperature. The curve for 90% reduction of area in Fig. 2 thus represents the onset of the same physical process, and the corresponding value of 15.2 k.cal./mole may therefore be more representative of the true activation energy. This figure is much smaller than the estimated value of 36–39 k.cal./mole usually quoted for self-diffusion and diffusion of solute atoms through the lattice of aluminium.

### Metallography

The specimens lying in the region of Fig. 1 beyond 60% reduction of area were subjected to a microscopic examination of deformed surfaces and of polished sections taken in the region of fracture. Specimens deformed at different temperatures were arranged in groups having similar values of reduction of area.

In each group, increase of temperature widens the average spacing of coarse slip bands and makes them more irregular in shape. Raising the temperature at the level of 60% reduction of area causes some increase in the extent of grain-boundary sliding and attempted migration, but grain-boundary migration is never free from the retarding influence of particles of a second phase at or near the original boundary. Grain-boundary sliding first



becomes apparent, at each temperature, as the value of reduction of area begins to fall from its maximum with decreasing strain rate. Intercrystalline cavities were observed near fracture in the surfaces of these specimens. As the figure for reduction of area falls, there is less tendency to neck at fracture, and more intercrystalline cracks become visible on the surface. No subgrains were observed in any of these specimens.

Specimens which fractured with less than 60% reduction of area showed no necking and contained many well-developed intercrystalline cracks, transverse to the stress axis, distributed throughout the gauge-length.

Examination of diamond-polished sections showed that specimens in the region of 90% reduction of area contained isolated intercrystalline holes. The majority of these holes occurred in the necked regions near the position of fracture, but some were present in the body of the specimen. The individual grains of the polycrystalline aggregate were severely elongated in the necked region, and the intercrystalline holes were similarly extended in the direction of tension. The appearance of these holes is therefore completely different from that of the typical intercrystalline cracks transverse to the stress axis. Increase of strain rate caused a reduction in the size and number of the isolated holes, and they tended to become confined to the region of the neck. However, it was not until the "transition strain rate" was exceeded by a factor of 4 or 8 that the holes were finally eliminated. No grain-boundary sliding was observed on the surface in this range of strain rate, and it is suggested that some incoherencies, developed between grains and precipitate, may have become enlarged by excessive local plastic deformation to form holes.

As the reduction of area fell (with decreasing strain rate), the intercrystalline cavities became larger and more numerous. Specimens with 60% reduction of area had large well-defined cracks lying transverse to the stress axis, but comparison showed that there was a tendency for large cracks to be close to the fracture at high temperatures, whereas they had a more general distribution at lower temperatures.

Specimens deformed at relatively slow rates with low reduction of area at fracture contain extensive intercrystalline cracks, some of which, as shown in Fig. 8 (Plate LXXVII), resemble the rows of disconnected holes found in the grain boundaries of copper,  $\alpha$ -brass, and magnesium by Greenwood *et al.*<sup>9</sup>

### The Grain-Size Effect

A considerable amount of work has already been done to show that, in general, an increase in temperature or decrease in strain rate causes increased participation of grain boundaries in creep deformation. In addition, a decrease in grain-size has been shown to result in an increased contribution of grain-boundary sliding to the overall deformation.

This feature was investigated in the aluminium-manganese alloy at 300° C. using specimens of two grain-sizes prepared from a fresh rolling batch of material. The normal cold-working and annealing procedure produced a grain-size of  $\sim 0.1$  mm. mean linear intercept. The larger grain size of  $\sim 0.5$  mm. mean linear intercept was produced by the normal annealing after cold work followed by 10% tensile strain and 2 hr. at 600° C.

The results are shown in Fig. 3. There is a pronounced displacement of the curve for larger grain-size to lower strain rates (the predicted direction). However, the possibility exists that this displacement may in part

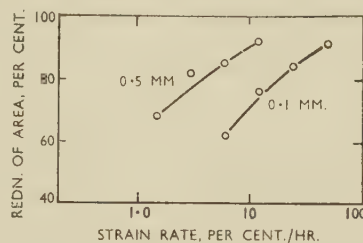


FIG. 3.—Reduction of Area Plotted Against Logarithm of Strain Rate for Specimens of the Aluminium-1½% Manganese Alloy of Two Different Grain-Sizes. Tested at 300° C.

be due to the different mechanical and thermal treatments used to produce the different grain-sizes.

### Part 2

A series of specimens of mean linear intercept 0.098 mm. (ranging from 0.090 to 0.107 mm.) was deformed to various creep elongations at 300° C. under constant-load conditions. A stress of 2500 lb./in.<sup>2</sup> was employed, which produced a minimum creep rate of 0.020%/hr. These specimens were taken from test at different stages of creep and fractured at room temperature. The values for reduction of area and elongation to fracture are plotted against creep elongation in Fig. 4. The curves suggest a gradual fall in reduction

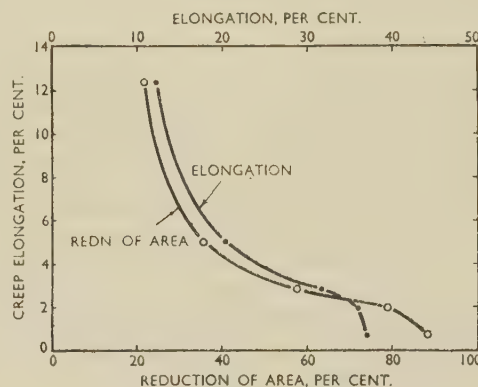


FIG. 4.—Creep Elongation Plotted Against Total Elongation and Reduction of Area after Fracture at Room Temperature for Specimens of the Aluminium-1½% Manganese Alloy Deformed under Constant Load at 300° C.

of area with increasing creep elongation until a point is reached where there is a sudden fall in ductility of specimens. This coincides with the end of steady-state creep.

A duplicate series of specimens was deformed to similar values of elongation and sectioned to reveal the state of crack development. After diamond polishing, small cracks were found in specimens corresponding to the end of the transient stage of creep. Cracks were quite well developed in specimens corresponding to the end of steady-state creep and the sudden fall in room-temperature ductility.

The test series was repeated at a constant strain rate of 0.025%/hr. The results obtained were similar in form to those at constant load, although they did not reproduce them numerically. Cracks were observed in specimens deformed to as little as 1.4% elongation, the sudden fall in ductility occurring at 2.5% elongation (Fig. 5).

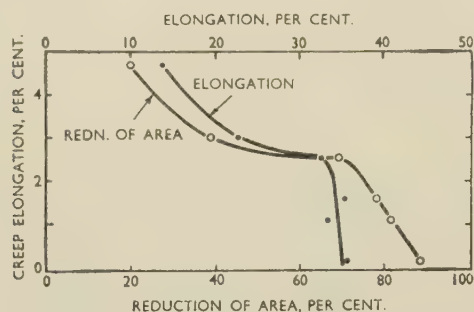


FIG. 5.—Creep Elongation Plotted Against Total Elongation and Reduction of Area after Fracture at Room Temperature for Specimens of the Aluminium-1½% Manganese Alloy (as Fig. 4) Deformed at Constant Strain Rate at 300° C.

These experiments show that intercrystalline cracks do form at a very early stage in the creep process and certainly within the secondary stage, an observation in agreement with the slight fall in density observed by Hanson and Wheeler<sup>3</sup> during this stage of creep in polycrystalline aluminium. At the beginning of tertiary creep, the cracks are sufficiently well developed to exert a marked influence on the room-temperature ductility of the specimens.

#### *The Form of Cracks*

In their early stages of formation, the cracks detected in diamond-polished sections often appeared as separate rounded holes, reminiscent of those observed by Greenwood. This type of appearance had also been found in specimens containing well-developed continuous cracks (Fig. 8, Plate LXXVII), but in those cases the removal of more material revealed a continuous crack in place of the disconnected holes. It was considered advisable to examine specimens by X-ray microradiography to ascertain whether the appearance of cracks in a two-dimensional section was really representative of their shape in three dimensions.

Thin sections were taken from the series of specimens deformed at constant strain rate. Each section, approximately 0.005 in. thick, was diamond-polished on both faces and examined by an X-ray method described by Betteridge and Sharpe.<sup>10</sup> Unfiltered cobalt radiation was employed.

In the first specimen in which holes were observed, both the diamond-polished section and the X-ray micrograph (Fig. 9, Plate LXXVII) showed separate rounded holes with no continuous cracks. A count taken over both faces of the original slice and over areas of the X-ray micrograph indicated that the latter showed a slightly higher density of holes than the former. This suggests that the X-ray micrograph had revealed some internal holes, though the evidence cannot be regarded as conclusive. The X-ray micrographs from specimens which had received greater creep elongations showed an in-

creasing proportion of continuous cracks, until eventually only a few separate rounded holes appeared (Fig. 10, Plate LXXVII).

In general, X-ray micrography and metallographic examination gave results in good agreement. Where agreement was not obtained, the X-ray micrograph indicated continuous cracks, but the microscope revealed separate rounded holes which on further polishing developed into continuous cracks. Care must be taken in basing any conclusions essentially on the appearance of separate rounded holes in microsections; X-ray micrography gives a much more reliable indication of the state of crack development.

#### *The Volume Fraction of Holes*

It has been suggested that the cracks in creep might be due to the accumulation of vacant lattice sites at grain boundaries.<sup>9</sup> It is not known whether vacancies would, under these conditions, migrate towards grain boundaries, nor whether they would coalesce to form stable voids at the boundaries transverse to the stress axis. Nor is it known whether the vacancies likely to exist in the metal are sufficiently numerous to account for the holes observed at various stages during the creep process. Two predictions of excess-vacancy concentration have been made, one being a hundred times larger than the other. The smaller, due to Seitz,<sup>11</sup> was based on changes in resistivity during cold work; the larger, by Mott,<sup>12</sup> relates to creep conditions.

Any attempt to correlate the predicted concentrations of vacancies with the volume of voids existing in the metal is subject to the limitation that, if vacancies do coalesce to form voids, at any instant there must be many voids too small to be seen. With this limitation in mind, the specimens previously used for X-ray microradiography were subjected to lineal analysis<sup>13</sup> to determine the volume fraction of visible holes at different stages of deformation. As the density of visible holes varied greatly from field to field, about fifty fields were examined and the results averaged. For each of three specimens which received less than about 3.5% creep elongation, the mean value of the volume fraction of visible holes was of the same order as, though less than, the volume of excess vacancies predicted by Mott. These results do not prove or disprove the vacancy-migration hypothesis; they merely show that it would be feasible if Mott's estimate is somewhere near the truth.

#### *Part 3*

The third part of the programme consisted of a series of tests to fracture at constant strain rate on specimens of the aluminium-magnesium alloy prepared in a similar manner to the previous specimens.

The grain-size of the aluminium-magnesium specimens is represented by a mean linear intercept of 0.57 mm./grain. The tests were conducted at 200°, 260°, and 300° C., and at strain rates of 0.2, 1.0, 10, 100, and 1000%/hr. The values of reduction of area are plotted against log. strain rate in Fig. 6. The curves reveal rather unusual behaviour, minima occurring at 300° and 260° C. in a central range of strain rate.

Intercrystalline cracking was observed in many of these specimens, and metallographic examination revealed the operation of such processes as coarse slip,



grain-boundary sliding, and boundary migration. The distribution, occurrence, and extent of such effects is shown in Table II. It can be seen that, in general, the

TABLE II.—Features Observed in Deformed Specimens of the Aluminium-5% Magnesium Alloy.

Temperature, °C.	Strain-Rate, %/hr.	Coarse Slip	Boundary Sliding	Boundary Migration	Intercrystalline Cracking
300	10 <sup>3</sup> 10 <sup>2</sup> 10 1.0	Extensive Moderate Diminished Fine slip	Slight Increased Moderate Extensive	None " Slight Extensive	Few examples Increased Extensive Elongated
260	10 <sup>3</sup> 10 1.0 0.2	Extensive Moderate Diminished Fine slip	None Considerable Increased Extensive	None Slight Increased Extensive	None Considerable Extensive Elongated
200	10 <sup>3</sup> 10 1.0 0.2	Extensive " Moderate "	None " Slight Considerable	None " " "	None " Present Considerable

incidence of intercrystalline cracking with decrease in strain rate is associated with the onset of grain-boundary sliding. The subsequent restoration of ductility to 100% reduction of area is associated with the beginning

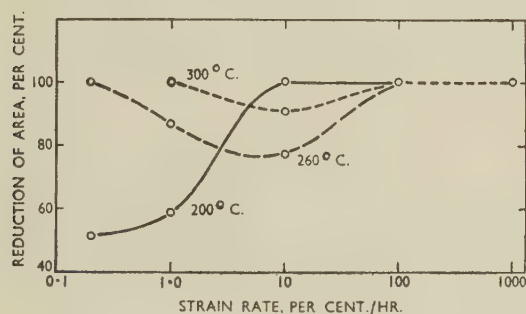


FIG. 6.—Reduction of Area Plotted Against Logarithm of Strain Rate for Specimens of the Aluminium-5% Magnesium Alloy.

of large-scale boundary migration, although some intercrystalline cracks were still present. Boundary migration was not observed on the surfaces of specimens deformed at 200°C., and there was no restoration of ductility within the lower limit of the range of strain rate employed.

#### Metallography

Diamond-polished sections taken from specimens of the aluminium-magnesium alloy employed in these tests were etched for 30 min. in a 10% aqueous solution of orthophosphoric acid. This etchant confers a dove-grey colour on the second phase in these binary alloys.

Specimens deformed to fracture at 300°C., that is, 30°C. above the solubility limit at this composition, showed no precipitate particles. In specimens fractured at 260°C. single-line networks of widely spaced particles were found precipitated along the grain boundaries. In some cases the particles were not laid on a smooth line, suggesting that some grain-boundary migration had occurred before nucleation and growth. Specimens tested for shorter periods contained fewer smaller par-

ticles, mainly confined to grain boundaries near the edges where grain-boundary sliding had obviously taken place. After fracture at 200°C. the grain boundaries were outlined by many small, closely spaced particles. In specimens deformed at the slower rates of 0.2 and 1.0%/hr., the particles occasionally outlined offsets at triple points. In a few cases the line had become expanded into a zone, 2-3 particles wide, suggesting that some restricted migration may have occurred whilst nucleation proceeded.

A section was taken from a specimen that had been given the standard annealing treatment of 24 hr. at 450°C. followed by 24 hr. at 260°C., followed by a further 24 hr. at 260°C., representing the time permitted to achieve thermal equilibrium before starting a test. No precipitation was found after this thermal treatment. This confirms that the precipitation observed at grain boundaries after test must have occurred during the period of plastic deformation at the test temperature. In addition, the nucleation and growth of precipitate particles appears to be encouraged by sliding displacement at grain boundaries.

The number and size of particles observed at different temperatures may be explained by a rise in rate of nucleation and a fall in rate of growth with falling temperature.

The intercrystalline cavities found in the aluminium-magnesium alloy are in general quite different from those occurring in the aluminium-manganese alloy. Cavities in the former material possess smooth outlines and have been widened by considerable sliding on longitudinal grain boundaries. Cavities in the aluminium-manganese alloy are usually narrow and irregular in shape. The difference may be attributed in part to the different relative smoothness of the boundaries in the two materials.

At some grain boundaries in the aluminium-magnesium specimens, rows of small rounded holes may be seen, reminiscent of some occurring in the aluminium-manganese alloy. In a few cases, where holes occur in boundaries which intercept the edge of the specimen, it is obvious that considerable boundary sliding has occurred (Fig. 11, Plate LXXVII). This throws light on a factor which has been neglected in arguments for the formation of intercrystalline holes by vacancy accumulation. The extent of grain-boundary sliding is often greater than the diameter of individual holes situated at boundaries. This means that the observed shape of holes subjected to boundary displacements of this order cannot be accepted as a guide to their mode of formation. The vacancy hypothesis of crack formation draws important conclusions from the rounded shapes of holes: this now seems to be a rather dangerous procedure. Crussard and Friedel<sup>14</sup> have advanced further criticism of such conclusions, suggesting that holes may change their shape by surface self-diffusion.

#### IV.—DISCUSSION

Two main hypotheses have been advanced to explain the occurrence of intercrystalline cracking in creep. These have been called the "stress-concentration" and "vacancy-migration" hypotheses.

## 1. STRESS-CONCENTRATION HYPOTHESIS

No precise model of the stress-concentration mechanism has yet been advanced. The general argument requires shear on grain boundaries inclined to the stress axis, causing a stress concentration on those boundaries perpendicular to the axis. Intercrystalline cracks should then form at the triple-points and propagate along the grain boundary. It seems likely that the formation of cracks by such a mechanism would require very high stresses, much greater than those experienced in practice. The application of higher stresses causes higher creep rates which usually discourage grain-boundary participation in creep. In addition, the majority of intercrystalline cracks formed during creep are not found at the triple-points.

Eborall<sup>15</sup> has discussed the arguments for a stress-concentration mechanism and concludes that little progress can be made until a more detailed model of the process is derived. He employs the concept of "relaxation" at the grain boundaries permitting relief of shear stress by sliding on those boundaries inclined to the stress axis.

Simple descriptions of a stress-concentration mechanism are inadequate because they do not explain the known temperature- and strain-rate dependence of intercrystalline cracking in creep. The modification suggested by Eborall is helpful, but does not overcome the need for a high stress to open and propagate intercrystalline cracks on transverse grain boundaries. The influence of boundary contour on sliding is ignored.

## 2. VACANCY-MIGRATION HYPOTHESIS

The vacancy-migration hypothesis was first proposed by Greenwood<sup>16</sup> to explain the formation at high temperatures and low strain rates of apparently disconnected round holes at grain boundaries in  $\alpha$ -brass. Similar features were later observed in copper and in magnesium.<sup>9</sup> Deformation within the grains was supposed to create an excess concentration of vacant lattice sites which diffused towards the grain boundaries. Those arriving at grain boundaries transverse to the stress axis would form groups stable under the applied tensile stress—the nuclei of intercrystalline cracks.

It is not known whether such groups of vacancies would be stable or whether sufficient numbers of vacancies are generated to account for the observed volume of holes formed. The influence of solute atoms and precipitate particles on this mechanism of crack formation would be difficult to envisage. Crussard and Friedel<sup>14</sup> have shown that it is unsafe to form conclusions concerning their origin from the shape of holes observed at grain boundaries during creep. Such reasoning was inherent in Greenwood's argument; he produced no evidence that any sort of diffusion process was operative.

It has been shown earlier in this paper that the volume of visible holes formed during the early stages of creep is less than the volume of the vacant sites predicted by Mott.<sup>12</sup> However, there is no definite information on the interaction of vacancies with dislocations at creep-test temperatures, and it is not known whether the vacancy lifetime is sufficiently long to permit a large proportion of them to reach the grain boundary.

It can be seen that the available evidence is insufficient to confirm the vacancy hypothesis. In its present form, it neglects the possible influence of grain-boundary sliding and migration on crack formation.

## 3. PROPOSED THEORY OF INTERCRYSTALLINE CRACKING

(a) *Basis of Fracture Behaviour*

The existing hypotheses have been shown to have considerable limitations. The present proposal is that there are two main processes operative in the mechanism of crack formation during creep. These are: (a) "relaxation" at grain boundaries, which permits boundary sliding; and (b) grain-boundary migration. The relationship between these two processes in any one material is believed to dictate fracture behaviour.

In a polycrystalline metal rapidly deformed at high temperatures, there is no grain-boundary sliding and no intercrystalline cracks form. According to the proposed theory, decrease of strain rate permits "relaxation" in the transition lattice, and boundary sliding occurs. The boundary interface is not smooth on the microscopic scale, and relative movement of the grains will establish both tensile and compressive stresses across different parts of it. Compressive stresses will cause plastic deformation in the adjacent material, but the maximum tensile stress which can be supported by the "relaxed" interface will be insufficient to deform the matrix, and intercrystalline holes will form. There are then two possibilities. If boundary migration is prevented, or occurs at very slow rates, intercrystalline holes will be produced as a direct consequence of grain-boundary sliding. Alternatively, if boundary migration occurs with sufficient freedom, no large holes will form. The surface of active boundary sliding moves into fresh positions, and the amount of sliding in each position is correspondingly reduced.

(b) *The Mechanisms Involved*

The proposed mechanism of crack formation depends upon the balance between grain-boundary sliding and grain-boundary migration under given conditions. Detailed models of these processes have been advanced by various authors.<sup>17-19</sup>

Beck *et al.*<sup>20</sup> have described a detailed model for grain-boundary migration in their discussion of the oriented growth of grains during recrystallization and coarsening. They ascribe this effect to anisotropy in the rate of grain-boundary migration. They assume that grain-boundary migration occurs by the departure of atoms from unfavourable (high-energy) positions on one lattice, their diffusion along the grain boundary, and their attachment to the other lattice at more suitable locations, the direction of transfer being dictated by strain-energy considerations. The essential role of boundary self-diffusion is apparent. The considerable influence of relative orientation of two crystals on the mobility of the boundary between them must be due to its influence on the rate of atom transfer across the boundary, and hence (we assume) on the rate of self-diffusion along the grain boundary. The experiments of Smoluchowski and his co-workers<sup>21-25</sup> have provided a considerable amount of



evidence for the anisotropy of grain-boundary diffusion (and self-diffusion). This provides direct support for Beck's proposed mechanism, if it is assumed that the rate of boundary migration is roughly proportional to the rate of boundary self-diffusion.

The proposed mechanism of crack formation can now be considered in greater detail. The "relaxation" of a grain boundary is ascribed to boundary self-diffusion. The rate of self-diffusion will increase with rise in temperature, but the degree of relaxation experienced at a given temperature depends on the strain rate imposed on the polycrystalline aggregate. At low strain rates, slow grain-boundary sliding may take place under fully relaxed conditions, when at very high strain rates the same rate of boundary self-diffusion would constitute an unrelaxed condition and no sliding would occur. The number of atom movements in self-diffusion per unit of strain appears to be the criterion of "relaxation".

According to Beck, grain-boundary migration is controlled by boundary self-diffusion, and on the basis of the present theory the processes of sliding and migration might be expected to operate together. It is possible that they do so, but the extent of migration may be too small to be observed if it encounters obstacles and is associated with considerable sliding. In practice, migration becomes obvious at strain rates below those at which sliding first appears. As the applied strain rate is reduced, the rate of shear imposed on grain boundaries decreases, and the time available for self-diffusion increases, so tending to encourage grain-boundary migration.

### (c) Application of Theory to Practice

The foregoing treatment assumes that there are no inhibitors of grain-boundary migration. In practice, it is found that particles of second phase, or impurities, or even etch pits situated at grain boundaries can retard migration by "anchoring" the interface. The behaviour of real metals and alloys may be interpreted by the effect of inhibitors on the relative ease and extent of grain-boundary sliding and migration, and by the relation between the rate of self-diffusion necessary to achieve relaxation and the corresponding permissible rate of grain-boundary migration.

In the aluminium-manganese alloy, the distribution of particles of second phase in the grain boundaries and throughout the grains exerts a sustained retarding influence on migration, even at the slowest strain rates. The boundary interface may escape from some particles, but it is immediately trapped by others in its path. Under these conditions, the extent of migration is very small, boundary sliding occurs on a confined interface, and intercrystalline cracks form. The fall in reduction of area with decrease in strain rate (Fig. 1, p. 482) is associated with the onset of grain-boundary sliding. The activation energy of 15.2 k.cal./mole derived from this graph is interpreted as the mean activation energy for relaxation at the grain boundary (achieved by boundary self-diffusion). Determination of the activation energy for grain-boundary self-diffusion in silver<sup>26</sup> shows that it is approximately half the value for lattice self-diffusion.<sup>27</sup> It is not known whether this rough relationship is valid for other metals, but the energy value derived from Fig. 1 is rather less than half the

activation energy for lattice self-diffusion of 34-39 k.cal./mole normally quoted for aluminium. The possible influence of the creep stress in lowering the activation energy for self-diffusion has not been considered.

According to the mechanism proposed by Beck,<sup>20</sup> the activation energies for grain-boundary self-diffusion and for grain-boundary migration should be identical, the former process controlling the latter at all temperatures. McLean<sup>28</sup> has reviewed the published data and shows that in general the experimental activation energy for grain-boundary migration is much larger than calculated values of the activation energy for boundary self-diffusion. In order to explain this anomaly, Burke<sup>29</sup> has proposed that at low temperature there are always sufficient insoluble impurities present to obstruct grain-boundary migration, but that these dissolve progressively with rise in temperature and exert less effect on migration. The result of this solubility change would be interpreted as an excessively large value of the activation energy for boundary migration.

Interpretation of the behaviour of the aluminium-magnesium alloy is complicated by the fact that at 200° and 260° C. nucleation and growth of precipitate is occurring at the grain boundaries during the course of the test. It is suggested that boundary self-diffusion and boundary sliding facilitate the onset of an otherwise sluggish precipitation process. At 300° C. there is no precipitate in this aluminium-magnesium alloy (although there may be equilibrium segregation), and the onset of sliding is followed by boundary migration. Some intercrystalline cracks do form, even at low strain rates, but they exert little or no effect on the reduction of area at fracture. At 260° C. there is a central range of strain rate in which the reduction of area falls appreciably, possibly owing to the inability of the grain boundary to escape from the fairly large, widely separated precipitate particles. At lower strain rates the grain boundary does escape, extensive migration occurs, and the reduction of area is restored to 100%, although some cracks are still present. At 200° C. the onset of grain-boundary sliding (at lower strain rate than at 260° C.) causes a fall in reduction of area which persists to low strain rates, and grain-boundary migration was not observed in these specimens. The precipitate consists of more numerous, smaller particles laid along the grain boundary, limiting the diameter of any cusp that might form and possibly making escape even more difficult (by analogy with dislocation theory).

In aluminium of 99.99% purity, the processes of sliding and migration seem to operate concurrently,<sup>30, 31</sup> indicating the absence of any inhibitor of grain-boundary migration. The behaviour of 99.99% copper is different in that it shows a transition from intercrystalline to transcrystalline fracture.<sup>8</sup> It is possible that the 0.01% of impurity retards grain-boundary migration more effectively in copper, or that the rate of migration permitted by a given rate of self-diffusion is inherently lower than in aluminium. This situation provides a more difficult test of the proposed theory, but it is essential for the success of the theory that such difficult cases be brought within its framework. In this respect a more thorough and extensive investigation of the metallography of creep in copper and other metals may be rewarding.

## ACKNOWLEDGEMENTS

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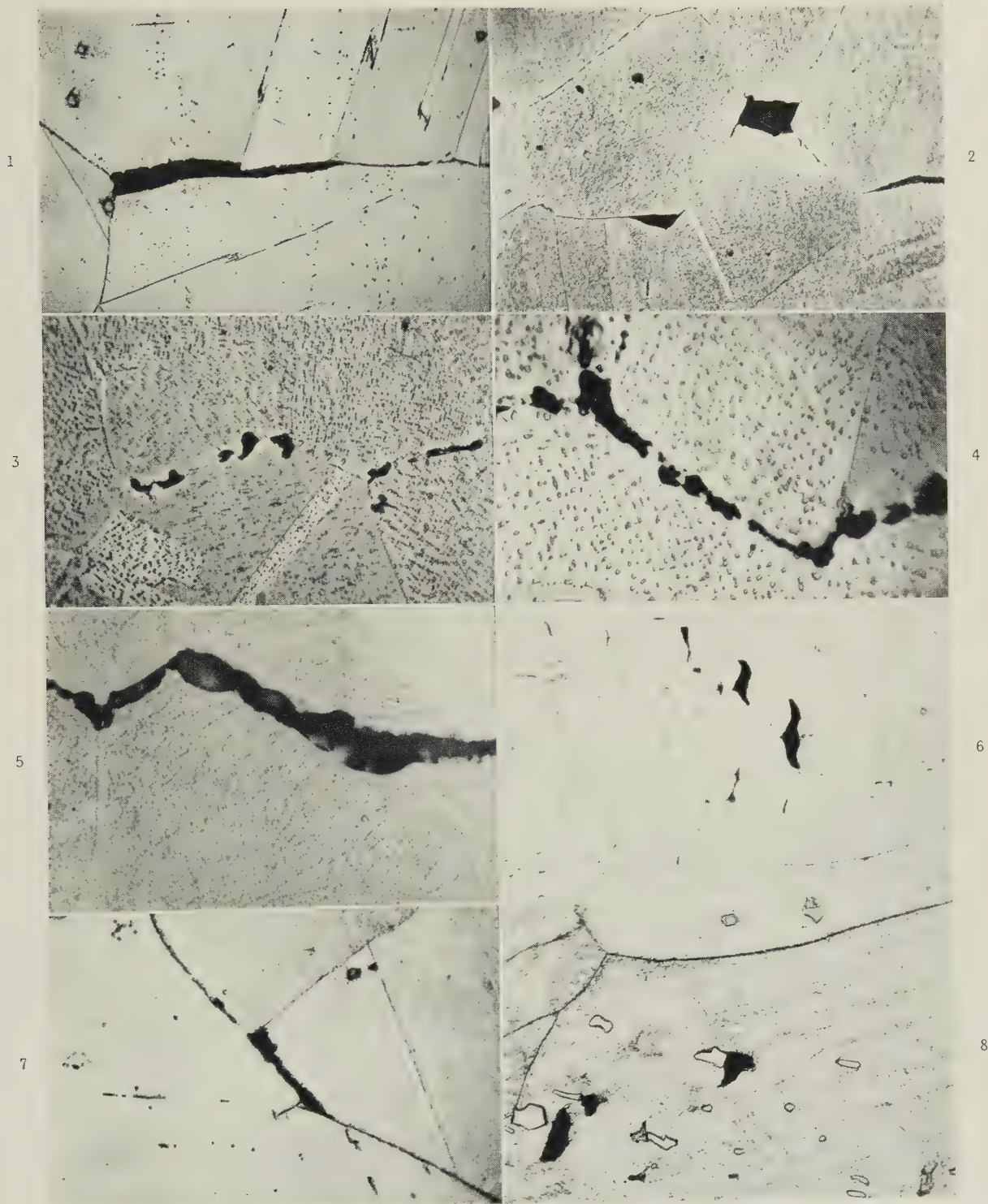


FIG. 1.—Wedge-Shaped (Type-*a*) Crack Based on Grain Corner. Nimonic 90 (specimen RSN 4C2) tested at 8 tons/in.<sup>2</sup> and 800° C. (2739 hr.).  $\times 500$ .

FIG. 2.—Same Specimen as Fig. 1. Cracks at both ends of a sliding boundary.  $\times 125$ .

FIG. 3.—Row of Cavities in Boundary Normal to Tensile Stress Axis. Nimonic 90 (specimen TPA 6C3) tested at 2½ tons/in.<sup>2</sup> and 900° C. (1900 hr.).  $\times 500$ .

FIG. 4.—Same Specimen as Fig. 3. Cavities beginning to link up.  $\times 1000$ .

FIG. 5.—Same Specimen as Fig. 3. Cavities fully linked up, producing type-*b* crack with wavy edges.  $\times 750$ .

FIG. 6.—Grain-Interior Cracks in Rex 337A (specimen RTE 7C6) tested at 20 tons/in.<sup>2</sup> and 700° C. (½ hr.).  $\times 250$ .

FIG. 7.—Crack Stopped at Twin Boundary in Nimonic 90 (specimen RSN 15C3) tested at 16 tons/in.<sup>2</sup> and 815° C. (42 hr.).  $\times 1000$ .

FIG. 8.—Crack at Inclusion in Rex 337A (specimen RTE 6C1) tested at 15 tons/in.<sup>2</sup> and 750° C. (5 hr.).  $\times 500$ .

Stress axis vertical for Figs. 1–5; horizontal for Fig. 6.

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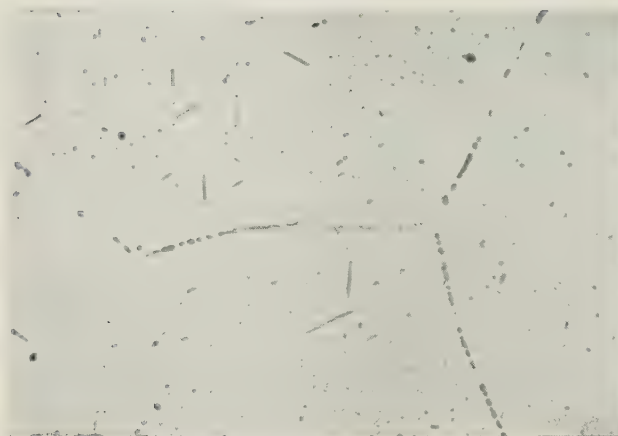


FIG. 1.—Structure of Nimonic 80A after  $\frac{1}{2}$  hr. at 1080° C. Following Solution-Treatment at 1225° C. and Overaging at 800° C.  $\times 1000$ .

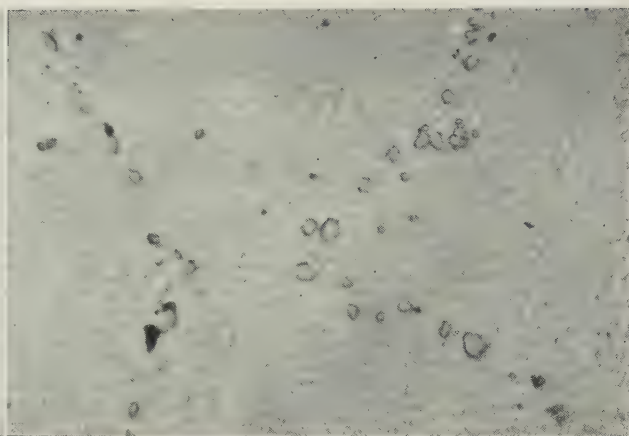
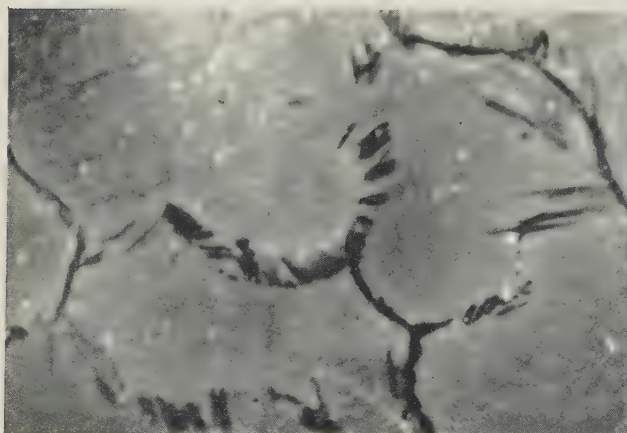


FIG. 2.—Structure of Nimonic 80A after 100 hr. at 1080° C. Following Solution-Treatment at 1225° C. and Overaging at 800° C.  $\times 100$ .



(a)



(b)

FIG. 3.—Microradiographs of Nimonic 80A,  $\times 150$ . (a) Chromium radiation; (b) iron radiation.



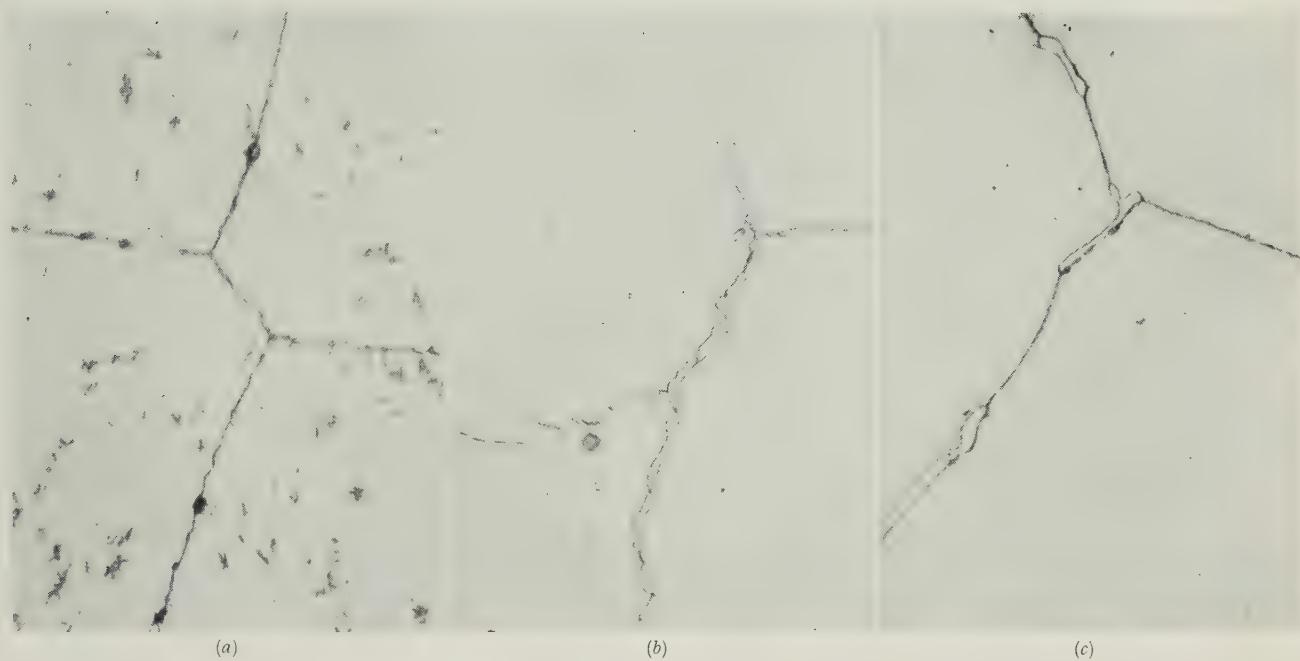


FIG. 4.—Influence of Intermediate-Treatment Temperature on Structure.  $\times 1000$ . (a)  $750^{\circ}\text{C}$ ., (b)  $950^{\circ}\text{C}$ ., (c)  $1075^{\circ}\text{C}$ .

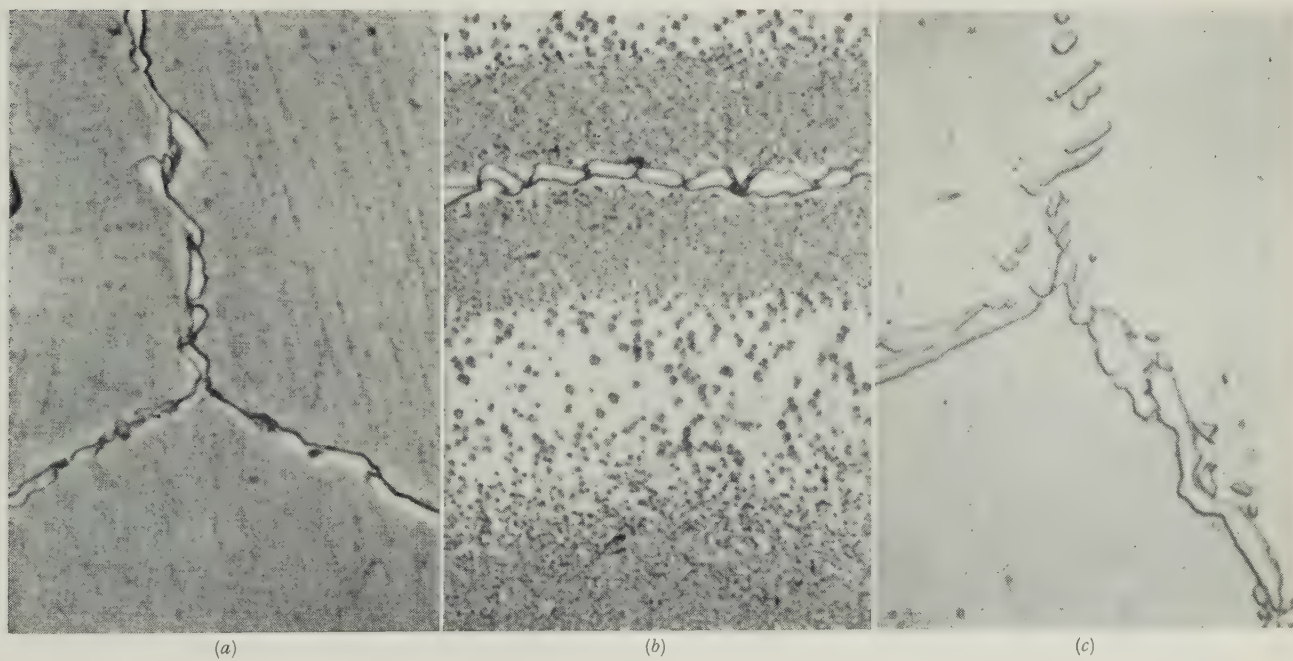


FIG. 5.—Influence of Ageing Temperature on Structure.  $\times 1000$ . (a)  $800^{\circ}\text{C}$ ., (b)  $850^{\circ}\text{C}$ ., (c)  $900^{\circ}\text{C}$ .

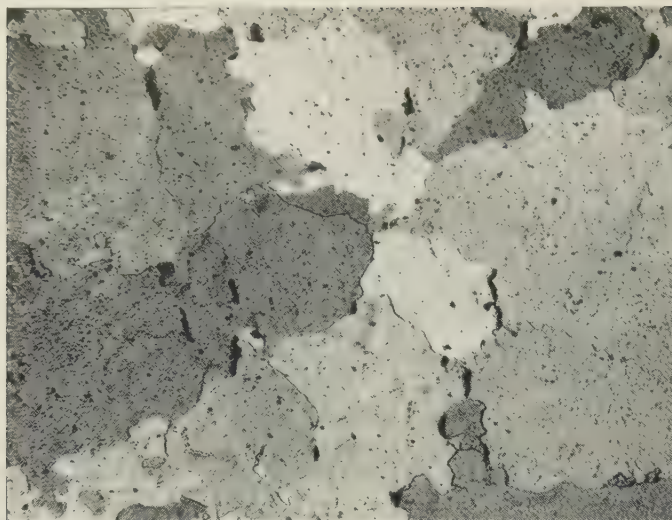


FIG. 7.—Aluminium-1 $\frac{1}{4}$ % Manganese Alloy. A diamond-polished section from a specimen deformed 10% in tension in 100 hr. at 300° C. Anodized and viewed under polarized light to produce grain contrast and reveal the intercrystalline nature of the cracks.  $\times 65$ .



FIG. 8.—Aluminium-1 $\frac{1}{4}$ % Manganese Alloy. A diamond-polished section from the same specimen as Fig. 7, showing intercrystalline cracks appearing as disconnected, rounded holes.  $\times 150$ .

FIG. 9.—Aluminium-1 $\frac{1}{4}$ % Manganese Alloy. An X-ray microradiograph of a thin section from a specimen deformed 1.4% in tension at 300° C. at a constant strain rate of 0.025%/hr. Small holes in the early stages of crack formation.  $\times 75$ .

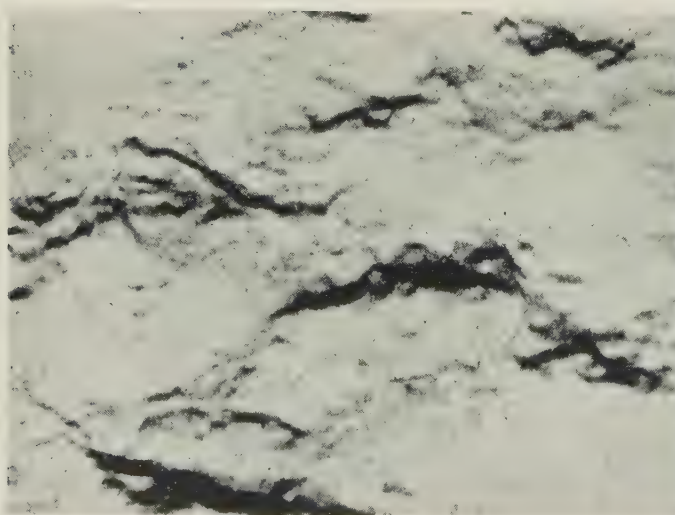


FIG. 10.—Aluminium-1 $\frac{1}{4}$ % Manganese Alloy. An X-ray microradiograph of a thin section from a specimen deformed 5.3% in tension at 300° C. at a constant strain rate of 0.025%/hr. Large continuous cracks at an advanced stage.  $\times 75$ .



FIG. 11.—Aluminium-5% Magnesium Alloy. A diamond-polished section from a specimen deformed to fracture at 200° C. at 1.0%/hr. showing intercrystalline cracks associated with considerable grain-boundary sliding.  $\times 75$ .

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# THE INTERNAL FRICTION OF PLASTICALLY DEFORMED COPPER \*

1779

By A. S. DARLING,† B.Sc.(Eng.), Ph.D., A.M.I.Mech.E., A.I.M., D.B.C.T., MEMBER

## SYNOPSIS

A torsion pendulum having a low background energy loss has been used to investigate the effect of plastic deformation upon the internal friction of tough-pitch and high-purity copper. The internal friction induced by deformation rises to a maximum for shear strains in the range 0.002–0.06 radian, after which it decreases rapidly. The magnitude of these effects increases with the temperature at which the specimen has previously been annealed. Secondary maxima on the internal-friction/strain curves appear to be associated with the presence of recrystallization textures.

The internal friction changes with time after straining. With copper of commercial purity, this change is invariably a decrease; with high-purity copper, the change may be either an increase or a decrease, and is dependent upon the specimen's history. The impurity level marking the transition from one type of behaviour to the other is approximately 0.004 wt.-%.

Changes of elastic modulus accompany these internal-friction changes, but are not directly related to them. The elastic modulus invariably increases with time after straining. The magnitude of the effect does not depend upon the impurity level, but is related to the prior annealing temperature.

The internal-friction effects induced by plastic deformation can be eliminated from tough-pitch copper, and considerably reduced in high-purity copper, by annealing at 160° C.

## 1.—INTRODUCTION

THE internal-friction effects induced by plastic deformation have been observed over the whole range of frequencies experimentally available, and no marked frequency-dependence has so far been reported. The mechanism responsible for energy dissipation must therefore be distinguished from those of other anelastic processes which occupy characteristic positions on the relaxation spectrum.

Lightly strained single crystals<sup>1–11</sup> vibrating in the kilo-cycle range of frequencies exhibit a strong amplitude-dependence which is characterized by a slight decrease of dynamic modulus at the higher vibrational strains. Such considerations led Nowick<sup>8</sup> to conclude that under these conditions energy is dissipated by a simple stress-hysteresis mechanism rather than by the more common relaxation processes.

Heavily strained single crystals do not exhibit this amplitude-dependence,<sup>12, 13</sup> and the effect has not been reported in connection with the behaviour of polycrystalline materials either lightly strained or heavily worked.<sup>14–17</sup>

The application of stress to annealed metal samples increases their internal friction, even though no measurable deformation occurs.<sup>1–11</sup> Such stresses result in increases of internal friction which are permanent at room temperature for cubic metals such as copper and transient for single crystals of hexagonal metals such as zinc or magnesium. If, however, samples of cubic metals are subjected to appreciable deformation, the internal friction produced has both permanent and transient components. This effect has been observed with both

single-crystal and polycrystalline material.<sup>15, 18, 12, 13</sup> The transient component, which may represent initially up to 70% of the total decrement, dies away at room temperature over periods of the order of 5–120 hr. after straining.

The permanent component can usually be removed by annealing at temperatures which do not affect the hardness or elastic coefficients. This effect has been commented upon by numerous workers, including Dorey<sup>19</sup> and Zener, Clarke, and Smith.<sup>16</sup> The efficiency of these low-temperature annealing processes appears to be critically related to the degree of deformation previously imposed. Found<sup>3</sup> reports, for example, that annealing at 100° C. halved the decrement of a single crystal of brass which had been strained longitudinally by 11%, whereas the decrement of a similar crystal which had been strained 2% was only slightly reduced by annealing at 825° C. for 3 hr.

Considerable uncertainty exists as to the shape of the curve of internal friction plotted as a function of strain. Köster, Bangert, and Lang<sup>20</sup> stated that the internal friction increased in a linear manner with degree of strain for reductions in area up to 98%. Previous workers, however,<sup>16, 17</sup> encountered well-defined maxima corresponding to critical strains on the internal-friction curve.

The present paper summarizes the results of a number of experiments carried out on polycrystalline samples of tough-pitch and high-purity copper. The work was undertaken to obtain more detailed information about the transient component of strain-induced internal friction, and to study the metallurgical factors affecting the shape of the curve relating internal friction with degree of strain.

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† Metallurgist, Johnson, Matthey and Co., Ltd., Research Laboratories, Wembley, Middlesex.





had been cast directly on to the concrete floor of the laboratory.

After being mounted in the apparatus, specimens were strained plastically in torsion by the rod (8) which passed through a Wilson seal (9) in the circular base-plate. This torsion bar could be rotated by a link mechanism (10), which was in turn moved by the screw-operated slide (11). This arrangement permitted a maximum axial twist of  $12^\circ$  to be imposed upon the specimen. For greater increments of strain, the link (10) was disconnected from

firmed that the background energy loss corresponded to a specific damping capacity not higher than 0.002%.

Fig. 3 also illustrates the constructional details of the furnace used for carrying out the low-temperature annealing treatments *in situ*. The furnace was split longitudinally, so that it could be assembled without disturbing the specimen. In use it was clamped round the top mounting flange, as shown in the diagram. The centre section of the specimen was heated by direct radiation from bare Nichrome elements inserted into slots which were moulded into the inner faces of two refractory formers. These were suspended, as shown, inside a nest of polished radiation screens.

TABLE I.—Impurity Concentrations in Materials Tested.

Element *	Weight Per Cent.	
	Tough-Pitch	High-Purity
Ag . . . . .	0.004	0.0002
Al . . . . .	0.0002	0
Fe . . . . .	0.0005	...
Mg . . . . .	<0.0001	...
Mn . . . . .	0.00005	0.0005
Ni . . . . .	0.003	0.0001
Pb . . . . .	0.005	0.0004
Si . . . . .	<0.0001	...
Bi . . . . .	0.0001	...
Cd . . . . .	<0.0001	...
Ca . . . . .	Trace	...
Na . . . . .	"	...
O <sub>2</sub> . . . . .	0.033	0.0012
N <sub>2</sub> . . . . .	0.0003	0.0021
H <sub>2</sub> . . . . .	0.00003	0.00003

\* Metallic impurities were determined spectrographically and the gaseous ones by vacuum-fusion methods.

the slide (11) and rotated by hand. Details of the specimens employed are given in Fig. 2.

Torsional vibrations were induced in the specimens by two small electro-magnets (13), with the aid of which a very gentle and symmetrical twisting action, which introduced no observable bending moments, could be obtained. The pole pieces of these magnets were situated approximately  $\frac{3}{4}$  in. from the centre-line of two mild-steel pegs on the inertia member. These pegs, which were diametrically opposed, also acted as supports for the stainless-steel mirror blocks (16).

The apparatus was completely covered with a steel bell-jar (14), which had a machined flange resting on the double-vacuum sealing rings shown. This bell-jar was provided in the front with a plate-glass window through which observations of the pendulum vibrations could be made. The complete assembly was evacuated by the diffusion pump (15), which was flange-mounted directly under the base-plate. Pressures in the vacuum chamber were measured with a McLeod gauge. Although usually below  $1\mu$  when the furnace was cold, the pressure frequently increased to 3–4  $\mu$  owing to the outgassing which occurred during the early stages of heating.

The method adopted for gripping the specimens is illustrated sectionally in Fig. 3. Split-steel bushes having a parallel bore and an external taper of  $2^\circ$  were drawn in corresponding tapers machined in the mounting flanges by the screws shown, thus firmly gripping the parallel shanks of the test-piece.

Preliminary tests carried out on the apparatus con-

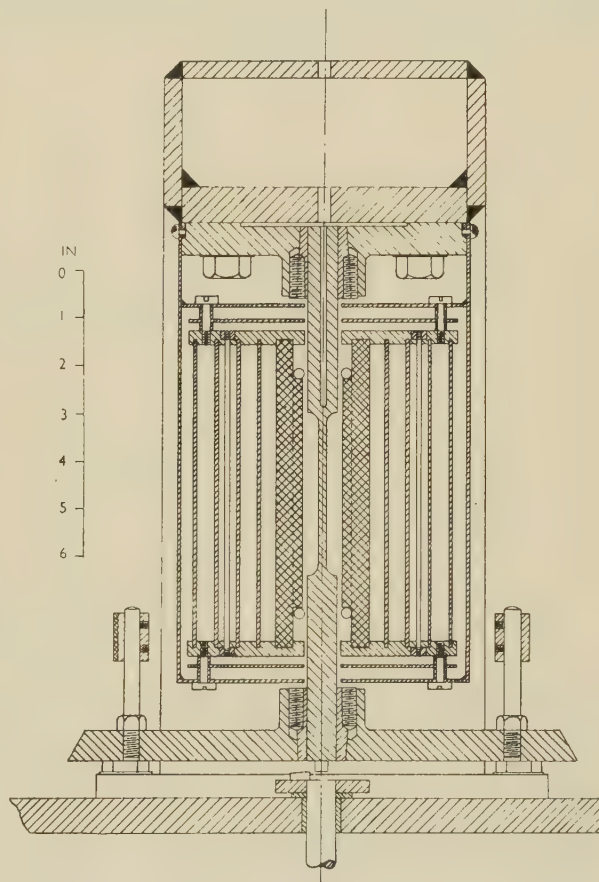


FIG. 3.—Sectional View of Specimen and Furnace Assembly.

The long parallel shanks of the specimens made it possible for the reduced centre section to be situated in a reasonably uniform temperature zone of the furnace. During vibration, the maximum elastic shear-strain energy stored in the reduced section of a specimen of this form is approximately 150 times greater than that stored in both the parallel shanks. Errors due to energy dissipation in the latter can therefore be neglected.

The top end of the specimen was drilled to accommodate a Chromel/Alumel thermocouple, the hot junction of which was in close proximity to the gauge-length of the specimen.

### 3. MEASUREMENT OF THE AMPLITUDE AND FREQUENCY OF VIBRATION

With specimens of the form adopted, surface shear strains of  $10^{-5}$  radian corresponded to an angular rotation of  $0.025^\circ$ . To measure rotations of this order, it was necessary to use a modification of the auto-collimator system. Fig. 4 illustrates diagrammatically the arrangement employed.

A stainless-steel block incorporating a plane aluminized mirror was mounted on one of the mild-steel pins upon which the electro-magnets operated. A block of identical size and weight was mounted on the other pin, so as to preserve the symmetry of the system and suppress any tendency towards the formation of subsidiary modes of vibration in the specimen.

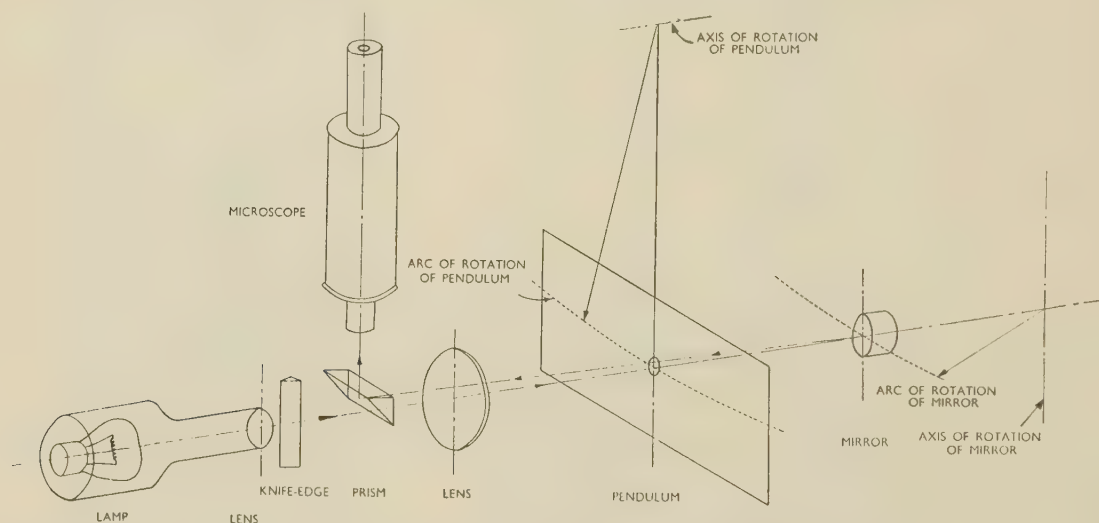


FIG. 4.—Strain- and Frequency-Measuring Equipment.

An image of the illuminated knife-edge was reflected back from the plane mirror on the inertia member and intercepted by the prism, so that it could be observed with the microscope shown. When correctly adjusted, the knife-edge divided the field of the microscope diametrically into light and dark areas. Vibration of the specimen caused the boundary between the light and dark areas to oscillate across the field, thus permitting the amplitude of vibration to be measured on an eye-piece scale.

Full-scale deflection at the eye-piece of the microscope corresponded to a shear strain at the surface of the specimen of  $2.5 \times 10^{-5}$  radian and strains as low as  $5 \times 10^{-7}$  could be accurately determined. The complete measuring assembly was fitted on guide rails, so that the movement of specimens submitted to increasing amounts of plastic strain could readily be followed.

Changes of the frequency of specimen vibration were measured very simply with the aid of a subsidiary compound pendulum which was mounted in front of the observation window of the bell-jar, as shown in Fig. 4. The bob of this pendulum acted as a shutter for the light beam from the auto-collimator. The  $\frac{1}{4}$ -in.-dia. hole in the bob was just large enough to permit the passage of a beam of light when the pendulum was stationary.

The period of the compound pendulum was adjusted to approximate closely to twice that of the torsion pendulum. When both pendulums were vibrating simultaneously the field of the microscope was illuminated for only a brief interval during each oscillation. The gradual progress of the image of the knife-edge across the field of vision could, therefore, easily be followed. The interval between successive passages in the same direction of the image of the knife-edge across the centre zero position on the eye-piece scale was inversely proportional to the difference in frequency of the two pendulums. This time interval could be accurately measured with a stop clock.

Accurate determinations of very small changes of frequency could be made by this technique. Frequencies employed in these experiments were in the

range 1–2 cycles/sec., and the compound pendulum was so adjusted that the time interval between successive coincidences was of the order of 100 sec. Under these conditions, a frequency change of 0.05% represented an alteration in the time interval of approximately 5 sec., which could be accurately measured. Frequency measurements made by this technique were accurate to within estimated limits of 0.02%.

### III.—EXPERIMENTAL RESULTS

#### 1. THE EFFECT OF DEGREE OF STRAIN ON THE INTERNAL FRICTION OF TOUGH-PITCH COPPER

Four specimens were examined. Three test-pieces were annealed for 2 hr. at  $300^\circ$ ,  $400^\circ$ , and  $600^\circ$  C., respectively. Heat-treatments were carried out in an atmosphere of oxygen-free nitrogen. The fourth test-piece was annealed for 16 hr. at  $850^\circ$  C. *in vacuo*. Control samples,  $\frac{1}{16}$  in. in dia., were heat-treated with each specimen and retained for subsequent X-ray and microscopic examination.

The results of grain-size determinations made on these control samples after heat-treatment are summarized in Table II.



The effect of annealing was initially to refine the rather large grain-size of the work-hardened material. Considerable grain growth occurred in the sample

TABLE II.—Grain-Size Determinations Made on Tough-Pitch Copper.

Annealing Time and Temp.	Mean Grain Dia., mm.
2 hr. at 300° C.	0.021
2 hr. at 400° C.	0.016
2 hr. at 600° C.	0.014
16 hr. at 850° C.	{ 0.62 large 0.046 small

annealed at 850° C. This process resulted in the formation of two distinct grain-size groups, the mean dimensions of which are given in the table.

*situ, in vacuo*, and the changes of internal friction with time and temperature recorded.

Fig. 5 illustrates the changes of internal friction which took place at room temperature after the application of various increments of strain to the specimen annealed at 600° C. The changes of frequency accompanying these changes of internal friction are shown in Fig. 6. These results are typical of all those obtained with tough-pitch copper. The figure associated with each of these curves indicates the total surface shear strain (in radians) to which the specimen had been subjected. The time axis of these graphs has been displaced longitudinally whenever necessary, in order to avoid confusion.

The internal friction of all the test-pieces examined decreased rapidly immediately after straining, whereas the frequency of vibration increased. Changes of frequency of this order of magnitude are greater than can

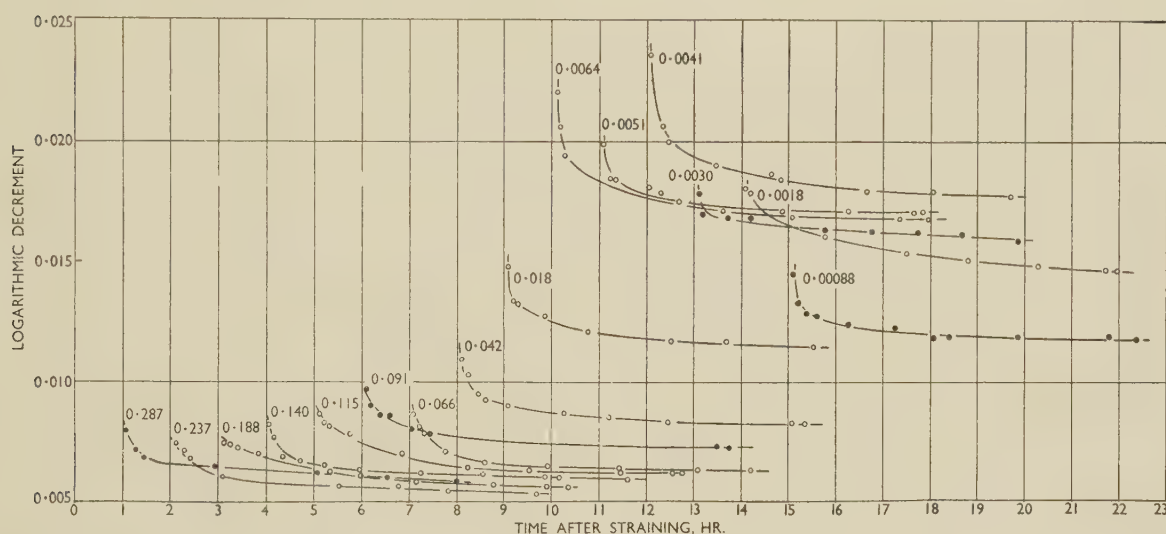


FIG. 5.—Changes of Internal Friction with Time After the Application of Various Increments of Strain to a Tough-Pitch Copper Specimen Previously Annealed at 600° C. Figures indicate total shear strain (radians) to which the specimen has been subjected.

After heat-treatment, the test-pieces were mounted in the apparatus and allowed to rest at room temperature for a day, in order that steady basic values for the internal friction and frequency of oscillation in the unstrained condition could be determined. They were then subjected to a small increment of torsional strain, after which measurements of the internal friction and frequency of vibration were made as quickly as possible. Subsequent measurements of the internal friction and frequency of vibration were taken at intervals over the next 7 or 8 hr., so that changes with time of these variables could be followed. Final determinations were made approximately 24 hr. after straining. A further increment of strain was then applied, and a similar series of readings taken.

Observations of this type were repeated until a permanent angular twist corresponding to a surface shear strain of approximately 0.3 radian had been applied to the specimen. At the conclusion of each programme of testing, the specimen was annealed *in*

be accounted for by the relationships between damping and resonant frequency dealt with in the theory of vibrations, in which the elastic modulus is assumed to remain constant. It is therefore not unreasonable to ascribe these changes to a gradual recovery of elastic modulus after straining.

Fig. 7 illustrates the internal friction of the four samples 24 hr. after straining, plotted as a function of total strain. Pronounced maxima occur on these curves at certain critical shear strains. In general, it can be concluded that the permanent increase of internal friction produced by an increment of strain increases with the temperature at which the specimen has been annealed. Secondary maxima on these curves occur at higher strains and extend over a wider strain range than the primary maxima.

Figs. 8 and 9 illustrate the curves of frequency plotted as a function of total strain for the samples annealed at 400° and 600° C., respectively. The general effect of increasing strain was continually to reduce

the elastic modulus. No rising trend was discerned for shear strains up to 0.3, though local minima occurred on the curves. These minima corresponded to the maxima on the internal-friction curves, showing that conditions of high permanent internal friction correspond to conditions of low elastic modulus.

Fig. 10 summarizes quantitatively the behaviour of the transient component of the internal friction. In this figure, the percentage change of internal friction per unit increment of strain which occurred within a given time after straining (2 and 24 hr.) is plotted as a function

specimen, and of the temperature at which it had previously been annealed.

The lower portions of the curves given in Fig. 10 are almost horizontal and show that the changes produced by small strain increments are remarkably sensitive to the magnitude of these increments. As the strain increments increase, their effects upon the proportional changes of internal friction progressively decrease. For shear-strain increments of 0.024 radian and above, the experimental curve approximates to one of inverse ratio, indicating that over this portion of the strain range the

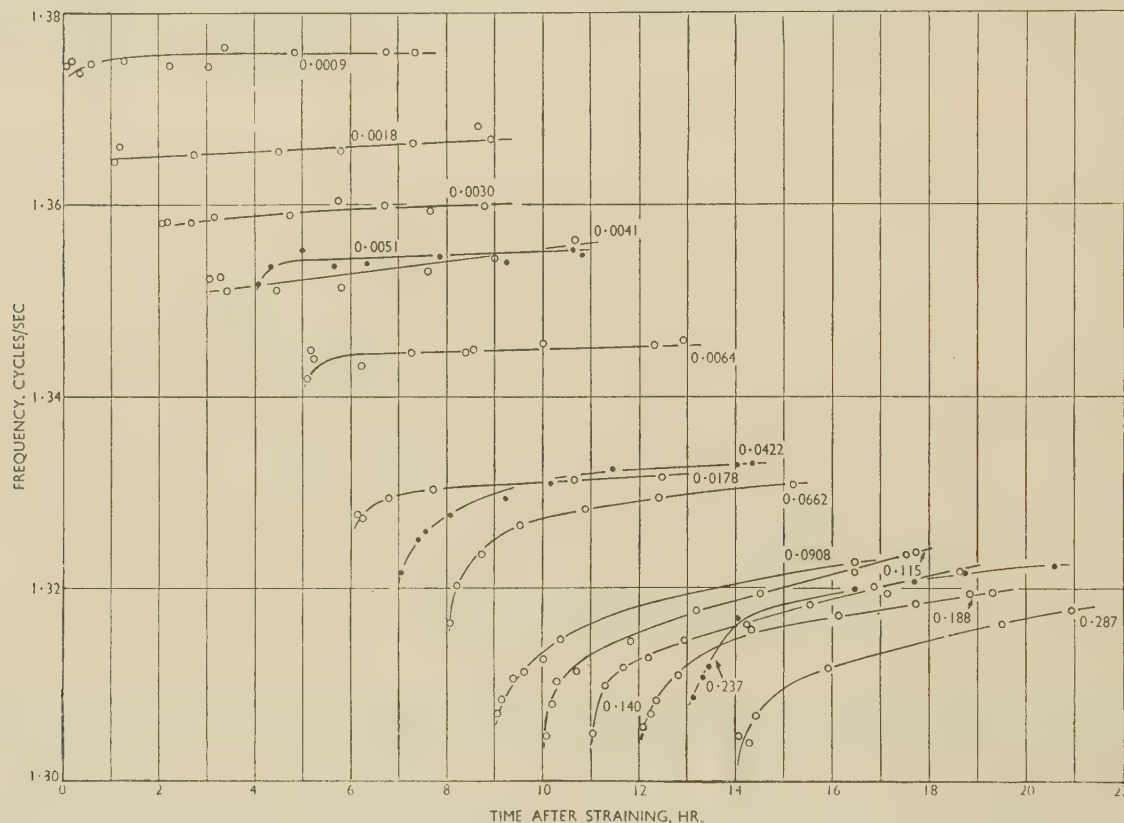


Fig. 6.—Changes of Frequency Accompanying the Changes of Internal Friction Illustrated in Fig. 5.

of the strain increment causing it. The extreme initial slopes of the internal-friction curves made it impossible to estimate the decrement immediately after straining. In order to calculate the proportional changes presented in Fig. 10, the decrement 5 min. after straining was taken as a reference value.

The experimental points for all four series of tests fell on a smooth curve for each time interval. These points were related only to the strain increment and were randomly distributed with respect to the total strain. It can therefore be concluded that the proportional changes of internal friction which occur within a given time after straining are affected only by the magnitude of the strain increment causing them. They appear to be independent of the total strain previously applied to the

proportional changes of internal friction are virtually independent of the strain increments causing them. The curves illustrating conditions 2 and 24 hr. after straining are both of similar form.

The proportional changes of frequency corresponding to the transient components of the internal friction discussed above are plotted against the strain increments causing them in Figs. 11 and 12. These curves illustrate that the changes of frequency are sensibly independent of the total amount of strain previously applied to the specimen, but are profoundly affected by the prior annealing temperature. The changes of frequency occurring within a given time after straining were, in the case of the specimen annealed at 600° C., approximately 50% greater than the corresponding changes in the





FIG. 7.—Internal Friction of Tough-Pitch Copper Specimens 24 hr. After Straining.

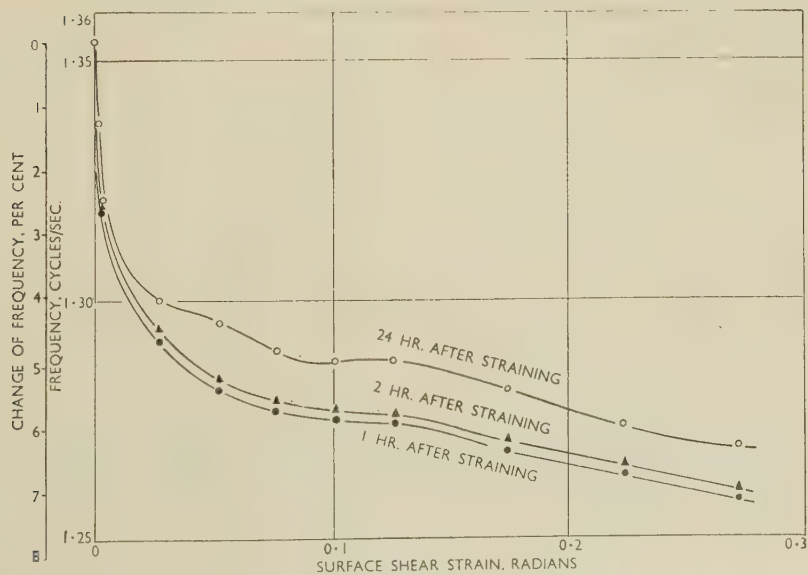


FIG. 8.—Frequency of Vibration of a Tough-Pitch Copper Specimen Previously Annealed at 400°C., Plotted as a Function of Applied Shear Strain.

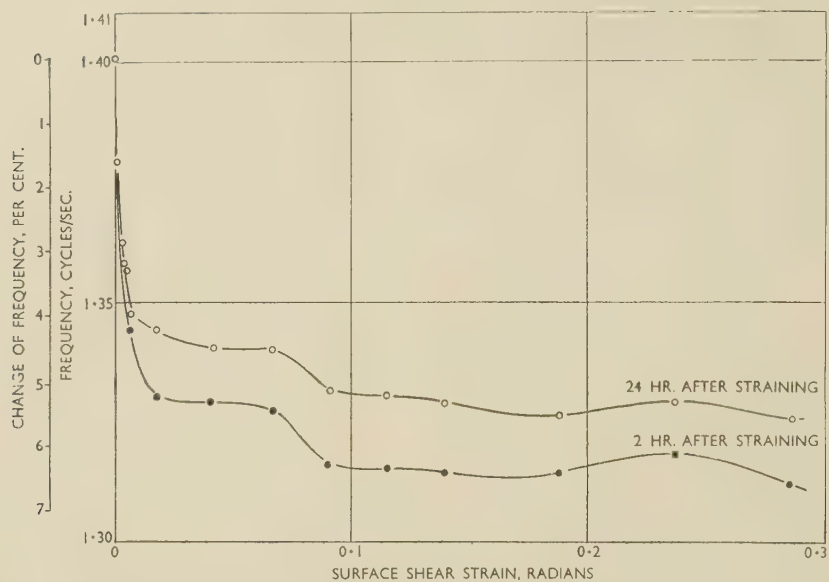


FIG. 9.—Frequency of Vibration of a Tough-Pitch Copper Specimen Previously Annealed at  $600^{\circ}\text{C}$ ., Plotted as a Function of Applied Shear Strain.

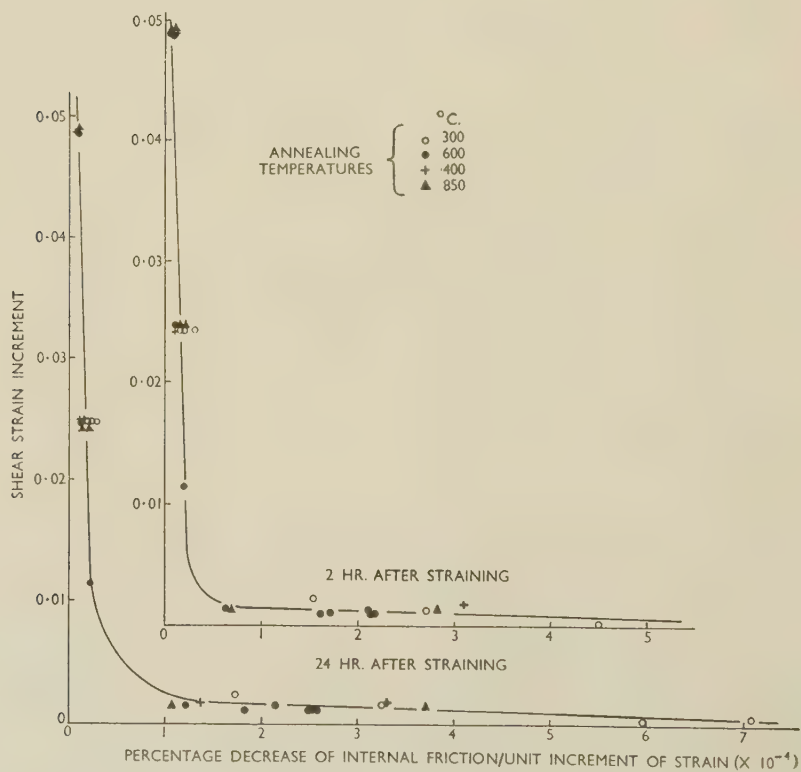


FIG. 10.—Proportional Changes of Internal Friction/Unit Increment of Strain, Plotted as a Function of Strain Increment. Conditions 2 and 24 hr. after the application of strain to tough-pitch specimens.



specimen annealed at 400° C. The results differed in this important respect from those of the internal-friction measurements.

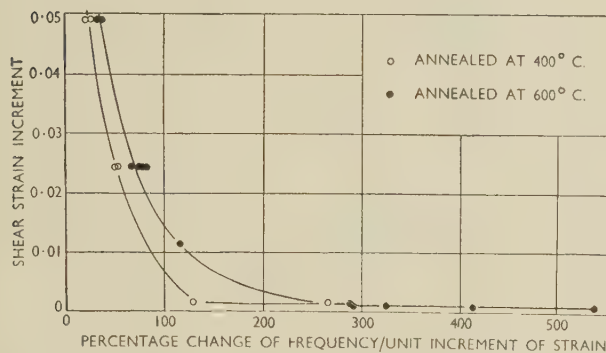


FIG. 11.—Proportional Changes of Frequency/Unit Increment of Strain, Plotted as a Function of Strain Increment. Conditions 24 hr. after the application of strain to tough-pitch specimens.

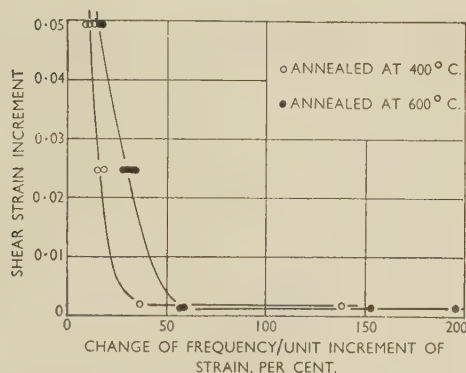


FIG. 12.—Proportional Changes of Frequency/Unit Increment of Strain, Plotted as a Function of Strain Increment. Conditions 2 hr. after the application of strain to specimens of tough-pitch copper.

## 2. THE EFFECT OF LOW-TEMPERATURE ANNEALING ON THE INTERNAL FRICTION OF STRAINED TOUGH-PITCH COPPER

Fig. 13 illustrates the effects of low-temperature annealing on the strained specimen originally annealed at 300° C. This curve is typical of many experimental results. Irregular heating curves, similar to that shown, were obtained in any experiment in which the effect was studied in sufficient detail. In view of the fact that the decrement decreased rapidly whenever the temperature was held constant, these irregularities were at first attributed to slight variations in the rate of heating. Further work will be required, however, to verify this hypothesis.

With reference to Fig. 13, the test-piece was heated from room temperature to 138° C. over a period of 6 hr. and held at this level overnight. Next day the temperature was rapidly raised to 152° C. and then gradually lowered to 59° C. over an 8-hr. period. The cooling portion of this curve was very smooth compared with that obtained with a rising temperature. Overnight

cooling reduced the temperature of the specimen to 17° C. Its decrement after this treatment was  $0.42 \times 10^{-3}$ .

The decrement of the specimen originally annealed at 850° C. was reduced to  $0.29 \times 10^{-3}$  as the result of a heat-treatment similar to that described above, and the decrements of all the strained samples of tough-pitch copper examined were reduced below  $1 \times 10^{-3}$  by annealing at temperatures not higher than 170° C.

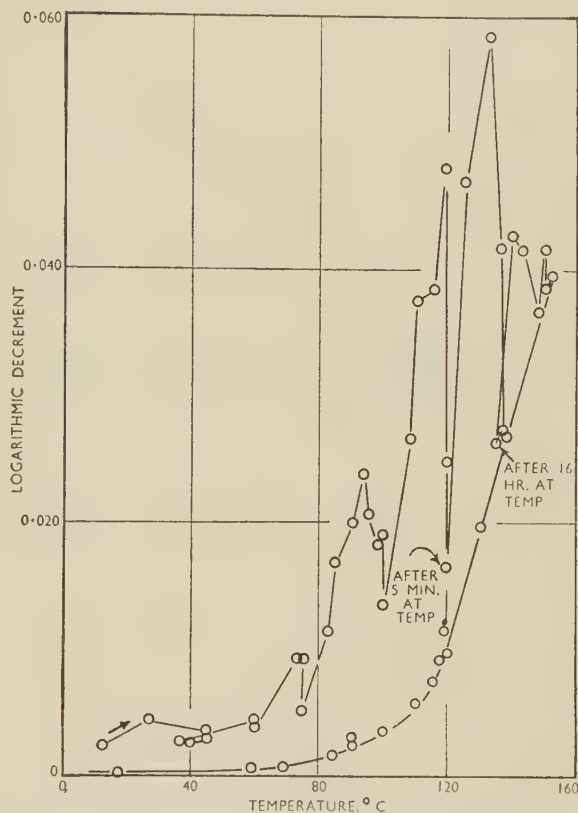


FIG. 13.—The Effect of Low-Temperature Heat-Treatment on the Internal Friction of a Strained Tough-Pitch Copper Specimen Previously Annealed at 300° C.

## 3. THE EFFECT OF DEGREE OF STRAIN ON THE INTERNAL FRICTION OF PLASTICALLY DEFORMED COPPER OF HIGH PURITY

Two test-pieces of this material were annealed in oxygen-free nitrogen for 2 hr. at 400° and 600° C. Control samples annealed at the same time as the specimens had mean grain diameters of 0.035 and 0.040 mm., respectively. The test-pieces were mounted in the apparatus after heat-treatment and subjected to a programme of straining and testing similar to that previously applied to the tough-pitch copper. In order to establish in greater detail the early relationships between internal friction and strain, smaller increments preceded larger ones in the sequence of testing.

Fig. 14 illustrates the changes of internal friction which occurred after the application of various increments of strain to the specimen annealed at 400° C.

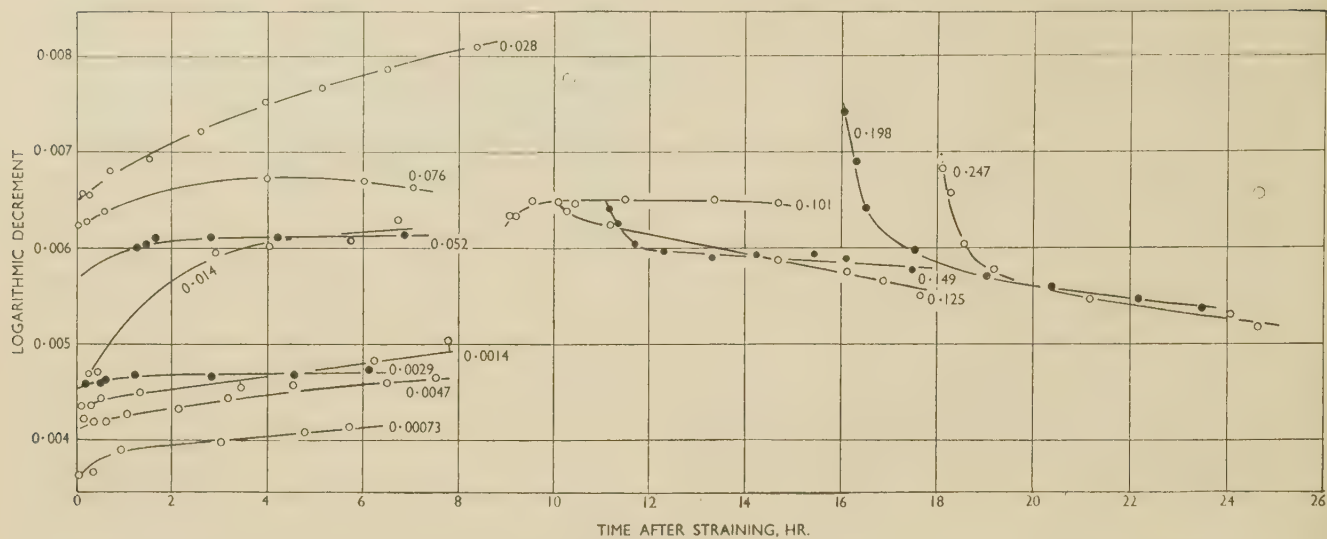


FIG. 14.—Changes of Internal Friction with Time After the Application of Various Increments of Strain to a High-Purity Copper Specimen Previously Annealed at  $400^{\circ}\text{C}$ . Figures indicate the total shear strain (radians) to which the specimen has been subjected.

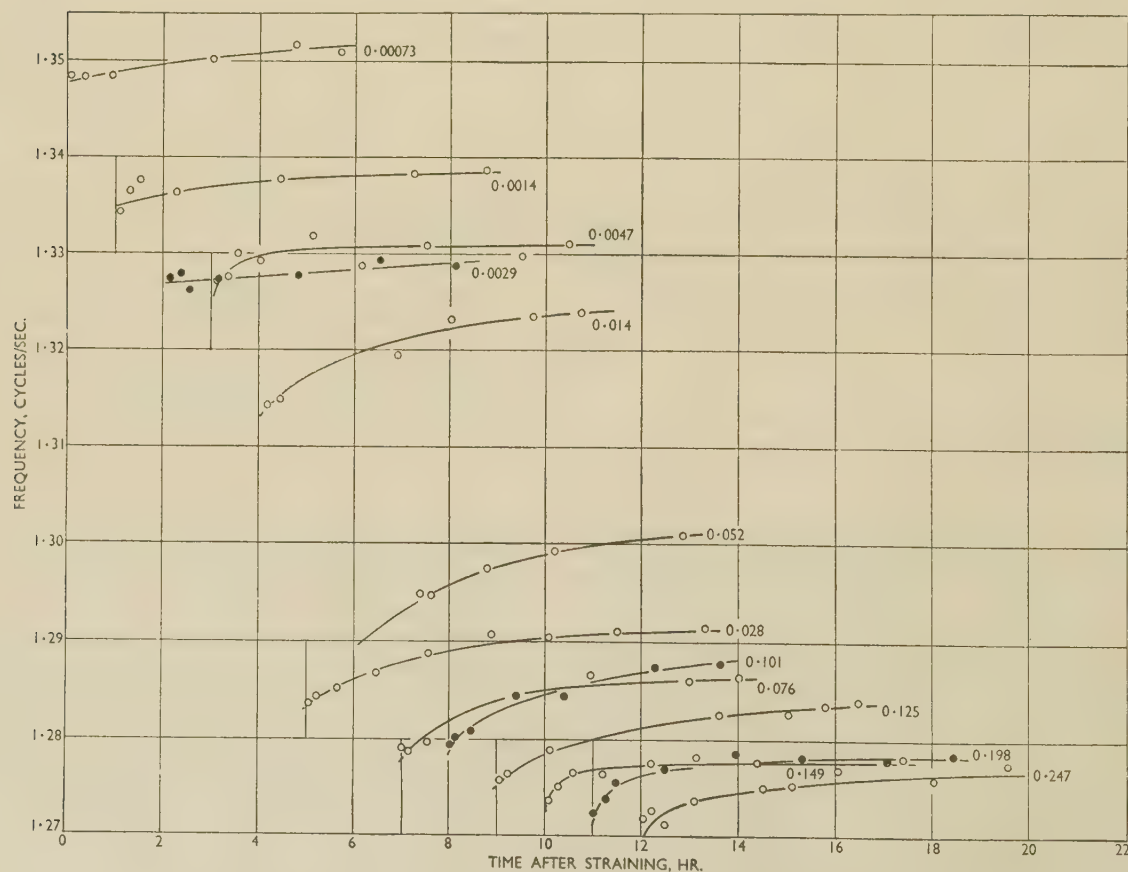


FIG. 15.—Changes of Frequency Accompanying the Internal-Friction Changes Illustrated in Fig. 14.



The essential feature of these graphs is that in the earlier stages of straining the internal friction increased with time, exactly the reverse behaviour of that previously exhibited by the tough-pitch copper. The curves corresponding to the intermediate ranges of strain are almost level, while those at higher strains show

related to the strain increments causing them by a curve similar to that in Fig. 10.

In Fig. 16 the internal friction 24 hr. after straining is plotted as a function of the total shear strain. Two maxima, corresponding to surface shear strains of 0.03 and 0.08, approximately, occur on this curve. The

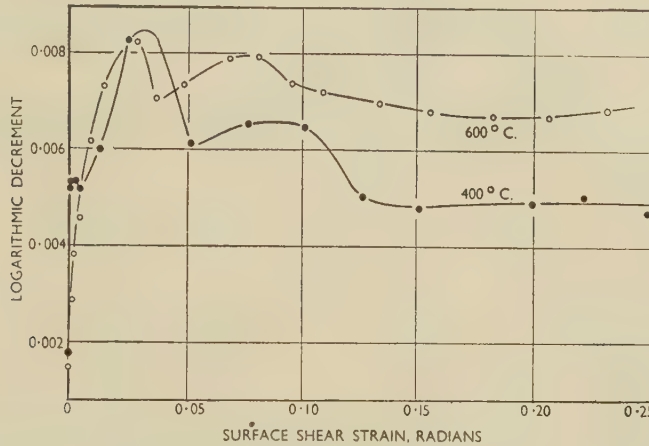


FIG. 16.—Internal Friction of High-Purity Copper Specimens 24 hr. After Straining.

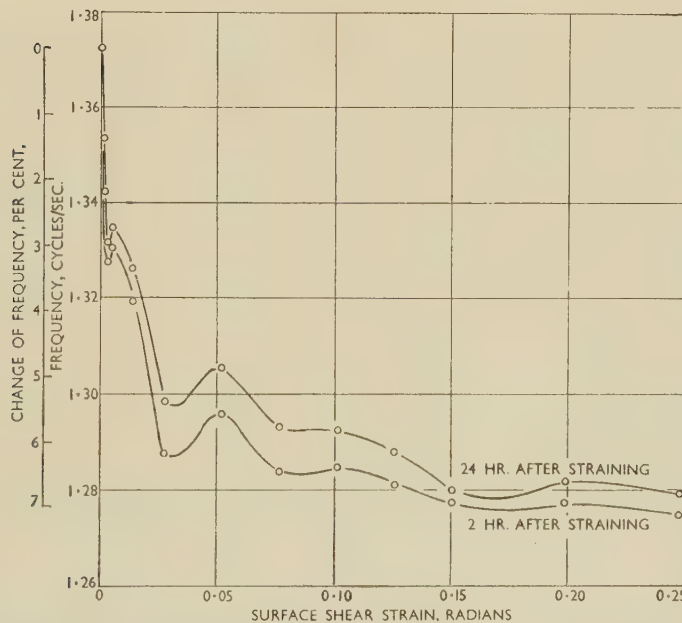


FIG. 17.—Frequency of Vibration of a High-Purity Copper Specimen Previously Annealed at 400° C., Plotted as a Function of Applied Strain.

an initial rapid decrease and are similar in general character to those of the tough-pitch copper.

The changes of frequency which accompany these changes of internal friction are illustrated in Fig. 15. These curves show that the frequency invariably increased with time after straining. The proportional changes of internal friction were not independent of the total strain applied to the specimen and could not be

major peak occurs at the lower shear strain and is narrower than the secondary maximum. An initial slight discontinuity on this curve corresponds to a shear strain of only 0.002 radian. The maxima on this internal friction curve have corresponding minima on the curve of frequency plotted as a function of total strain (Fig. 17).

Curves showing the changes of decrement with time

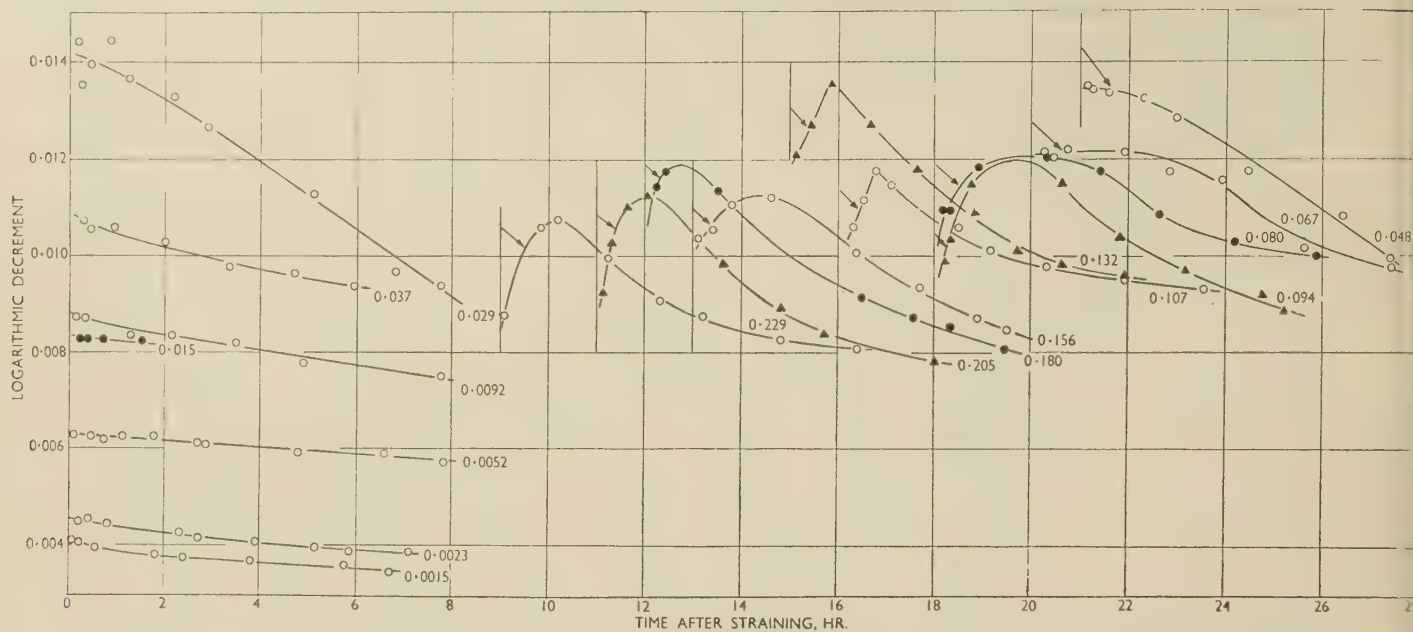


FIG. 18.—Changes of Internal Friction with Time After the Application of Various Increments of Strain to the High-Purity Copper Specimen Previously Annealed at 600° C. Figures indicate the total shear strain (radians) to which the specimen has been subjected.

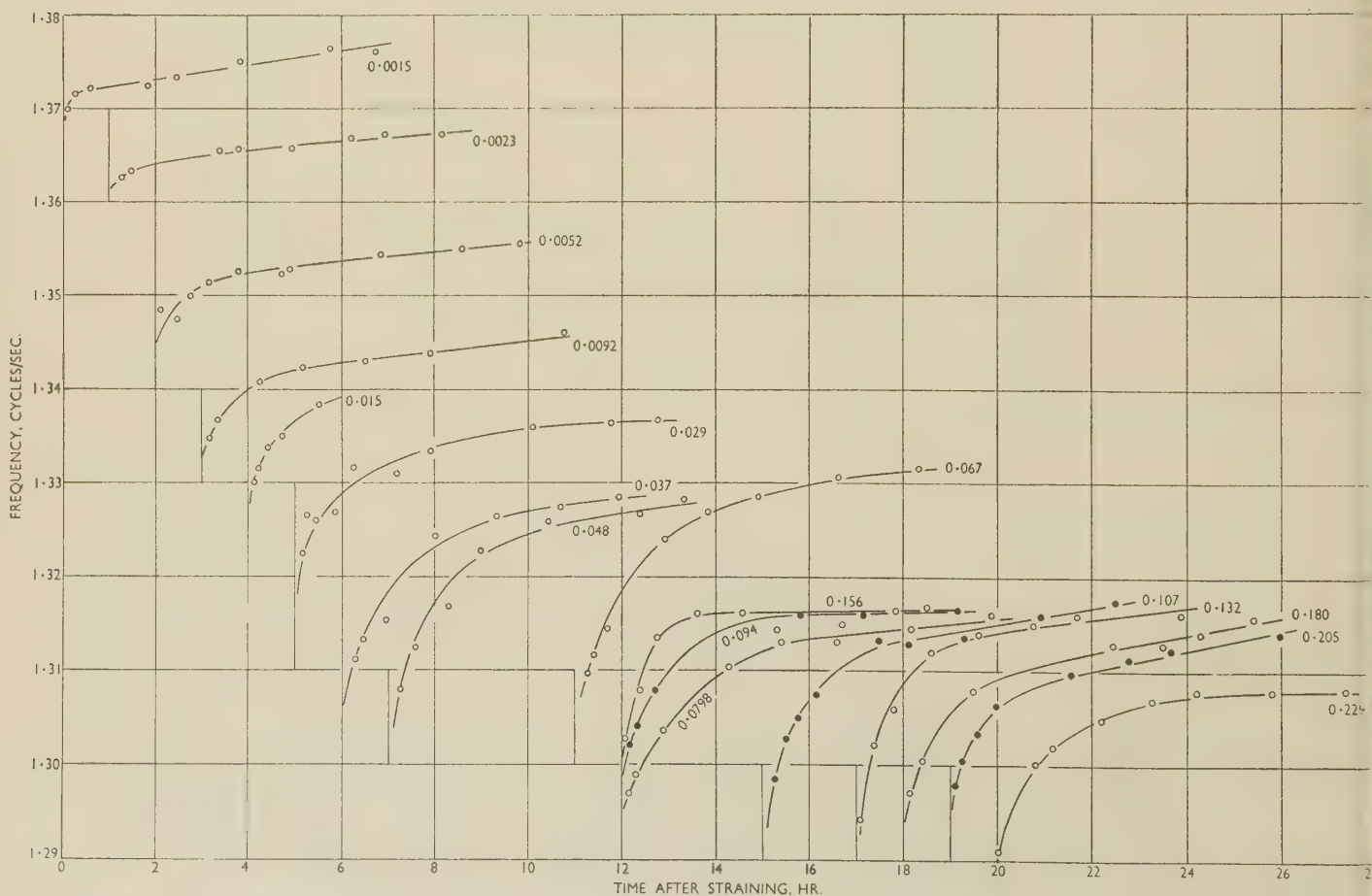


FIG. 19.—Changes of Frequency Accompanying the Internal-Friction Changes Illustrated in Fig. 18.



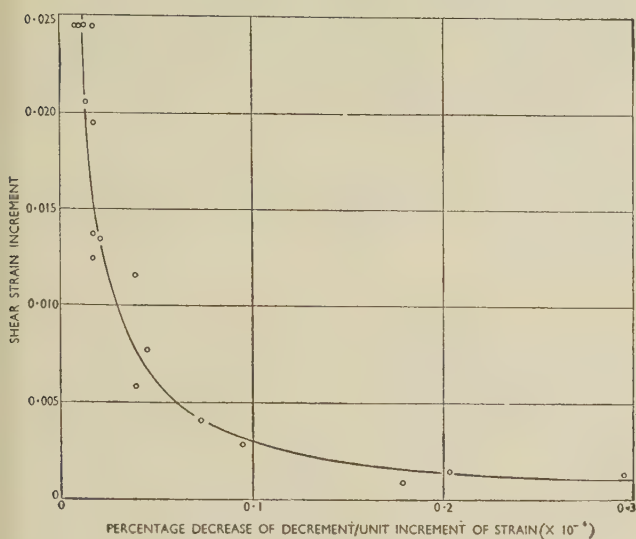


FIG. 20.—Proportional Changes of Internal Friction Occurring After the Application of Various Increments of Strain to High-Purity Copper Specimens Previously Annealed at 600° C., Plotted as a Function of Strain Increment. Conditions 24 hr. after the application of strain.

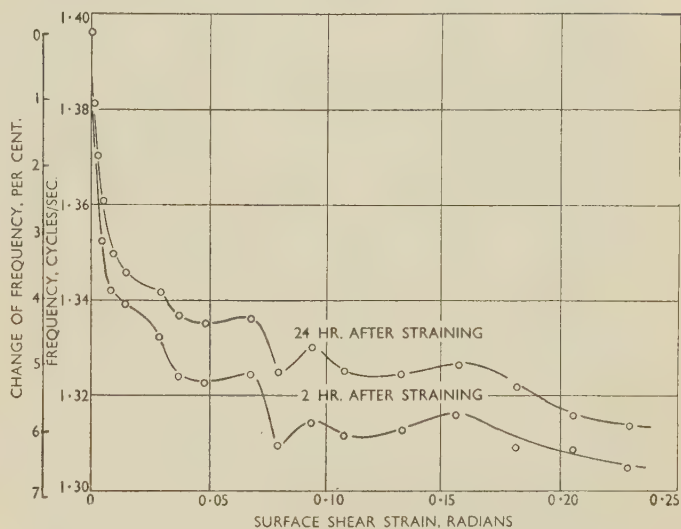


FIG. 21.—Frequency of Vibration of High-Purity Copper Specimen Previously Annealed at 600° C., Plotted as a Function of Applied Strain.

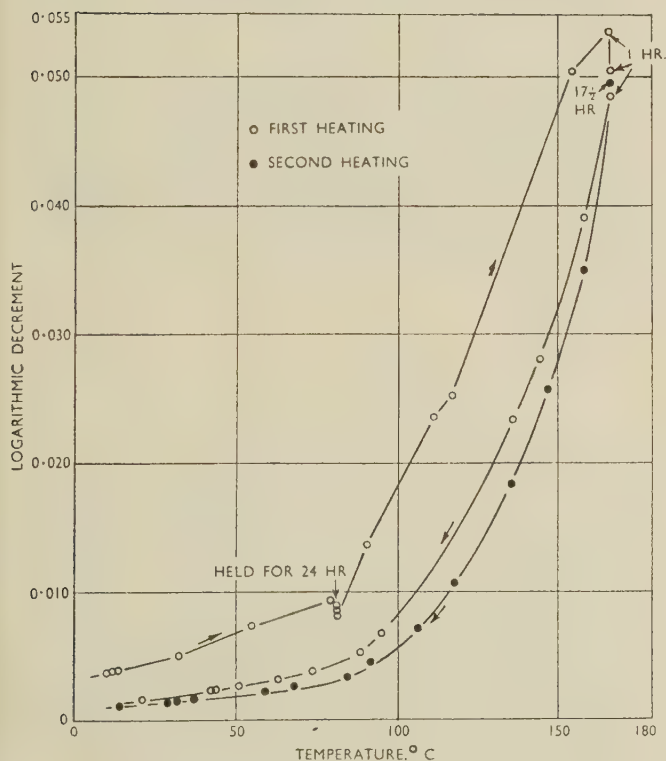


FIG. 22.—Effect of Low-Temperature Heat-Treatment on the Internal Friction of a Strained High-Purity Copper Specimen Previously Annealed at 400° C.

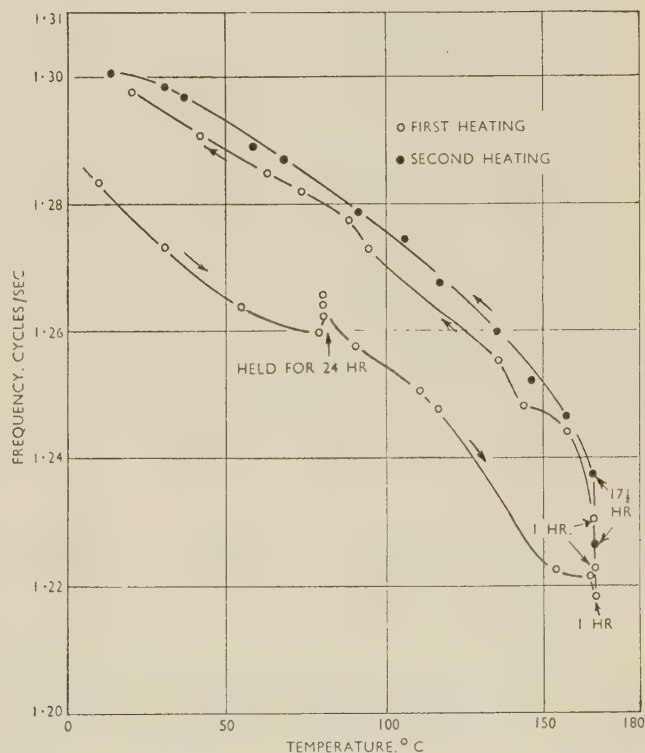


FIG. 23.—Effect of Low-Temperature Heat-Treatment on the Frequency of Vibration of a Strained High-Purity Copper Specimen Previously Annealed at 400° C.

for periods of approximately 8 hr. after the application of various increments of strain to the specimen previously annealed at 600° C., are presented in Fig. 18. These curves differ not only from those previously obtained with tough-pitch copper, but also from those of the high-purity sample annealed at 400° C. After the application of small strain increments at the lower end of the strain range, the internal friction decreased very slowly with time. As the total strains increased, the initial part of these curves tended to level off, and still higher applications of strain resulted in curves exhibiting an initial rapid rise of internal friction with time.

Fig. 19 illustrates the frequency changes accompanying these effects. These frequency changes were of the standard type observed with all the specimens previously examined.

The behaviour of the transient component of the internal friction of this specimen was easier to interpret than that of the previous sample. The proportional changes of decrement which occurred in a period of 24 hr. after the application of strain were found to depend primarily upon the magnitude of the strain increments causing them (Fig. 20).

Owing to the sudden initial increases of decrement which occurred towards the higher end of the strain range, conditions 2 hr. after straining were rather more complex and not susceptible to simple graphical representation.

The internal friction 24 hr. after straining is plotted in Fig. 16 as a function of strain. The effects produced by straining were slightly greater in magnitude than those of the sample annealed at 400° C. An interesting feature of the two curves is that the ratio of the strains corresponding to the maximum values of primary and secondary maxima are in both cases the same. The maxima of the internal friction curve have corresponding minima on the curve of frequency plotted as a function of total strain (Fig. 21).

The proportional changes of frequency corresponding to the transient components of the internal friction of both these pure copper test-pieces were similar to those of the tough-pitch copper illustrated in Figs. 11 and 12. They were independent of the total strain applied to the specimen, but were affected by the temperature of previous annealing. The proportional frequency changes of the specimen annealed at 600° C. were approximately twice those of the specimen annealed at 400° C.

#### 4. THE EFFECT OF LOW-TEMPERATURE ANNEALING ON THE INTERNAL FRICTION OF STRAINED COPPER OF HIGH PURITY

Figs. 22 and 23 illustrate the effect of low-temperature annealing on the strained specimen previously annealed at 400° C. The specimen was rapidly heated to 81° C. and held at this temperature for 24 hr. It was then slowly heated to 166° C., held for 1 hr., and finally cooled slowly to room temperature. The decrement at 20° C. was  $1.5 \times 10^{-3}$ , a value higher than expected in view of the previous work on less pure material. Further annealing at 166° C. for 17 hr., followed by slow cooling, reduced the decrement at room temperature to  $1.06 \times 10^{-3}$ .

The frequency changes which occurred during these annealing processes are illustrated in Fig. 23. Discontinuities occurring on the internal-friction curve are faithfully reflected on the frequency curve. In spite of the partial elastic recovery that occurred, the final frequency of 1.302 cycles/sec. was still 4.6% lower than the unstrained value.

Annealing for 1 hr. at 166° C. reduced the internal friction of the specimen previously annealed at 600° C. to  $1.06 \times 10^{-3}$ , a value identical with that of the previous sample which had been annealed at 166° C. for a total period of 18 hr.

#### 5. X-RAY WORK

Small triangular prisms were sawn from the longitudinal axis of control samples which had been annealed at the same time as the test-pieces. These prisms were etched into needles approximately 0.3 mm. in dia. and mounted in a 6-cm. single-crystal camera. The longitudinal axis of these needles, about which they were continuously rotated during exposure, was perpendicular to the X-ray beam.  $\text{CuK}\alpha$  radiation was employed.

The diffraction patterns obtained indicated that preferred orientations existed in the materials tested. A pronounced double-fibre texture existed in both grades of copper in the work-hardened, as-received condition. The strongest texture was due to crystals having their [111] direction aligned with the specimen axis. The [100] texture, although weaker, was still well defined.

Annealing the tough-pitch copper at 400° C. for 2 hr. left only a very weak [100] alignment. Growth of the [111] texture after annealing at 600° C. resulted in further weakening of the 400 and 420 lines and complete elimination of the [100] texture. Annealing at 850° C. increased even further the intensity of the [111] alignment.

Both [111] and [100] alignments were present, although not pronounced, in the high-purity specimen annealed at 400° C. Annealing at 600° C. resulted in an increase in the intensity of the [111] texture and a greatly decreased [100] alignment, which was almost destroyed by this treatment.

### IV.—DISCUSSION OF RESULTS

#### 1. SHAPE OF THE CURVES OF INTERNAL FRICTION PLOTTED AS A FUNCTION OF STRAIN

In a general way it is easy to appreciate why the internal-friction curves should exhibit a major peak corresponding to a critical shear strain. Nowick<sup>22</sup> has put forward an explanation based on the virtually instantaneous movement of dislocations under stress in accordance with his static-hysteresis hypothesis. Similar considerations will, however, apply whether the movement is instantaneous or dependent upon thermal activation. Energy dissipated at any stress will be proportional to the integrated movement of all the dislocations which contribute to the non-elastic strain component.

Although the total number of dislocations will increase with degree of strain, their relative mobility will decrease. The situation can be represented in a rudimentary fashion by Fig. 24. Here, curve (a) represents the degree of movement under any given shear stress, and curve (b)



the total number of dislocations. The third curve, giving the product of quantities (a) and (b), resembles in general character many of the curves obtained in the present research. Similar curves were obtained by Hasiguti and Hirai<sup>12</sup> with single crystals of copper.

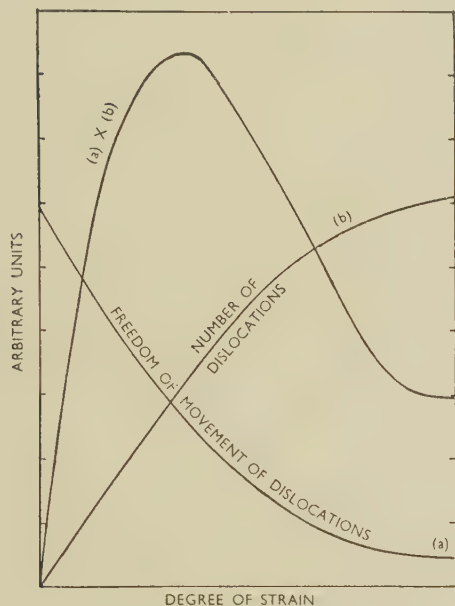


FIG. 24.—Diagrammatic Representation of the Increase in Number, and Decrease in Mobility, of Dislocations in a Specimen Subjected to an Increasing Amount of Plastic Strain.

In order to account for the secondary maxima on the curves shown in Figs. 7 and 16, it becomes necessary to consider preferred orientations in the recrystallized material. Energy dissipated during vibration by the specimen as a whole will be the sum of energy losses in individual grains. The internal friction of these grains

will be uniquely related to the sum of the shears to which they have been subjected, rather than to a strain calculated simply from some external change of shape or dimension. The internal friction of a polycrystalline aggregate will therefore depend upon the shear-strain history of the individual grains of which it is composed.

For purposes of the present discussion, it can be assumed that the sum of the shears to which individual grains are subjected is proportional to the external shear strain applied to the specimen. This constant relationship between internal and external strains will in turn be a function of the orientation of the crystal with regard to the direction of the applied shear. When a specimen having two predominant orientations is subjected to a gradually increasing shear strain, grains corresponding to each alignment will pass through their internal-friction maxima at different external degrees of strain. These conditions can be represented diagrammatically by the curves shown in Fig. 25. Here curves (a) and (b) represent the contributions to internal friction of grains having two distinct orientations with respect to the direction of the applied strain. The relative magnitude of the two components will depend upon the proportion by volume of grains having these alignments and will therefore be directly related to the intensity of the fibre texture. The upper curve in Fig. 25, representing the sum of curves (a) and (b), is similar in general character to the experimental curves shown in Figs. 7 and 16.

It seems reasonable, therefore, to associate the secondary maxima on the experimental curves with the presence of preferred orientations in the materials tested. In view of the X-ray evidence, it is considered that the shape of the internal-friction curves in Fig. 7 is due to the superposition of a maximum caused by the [111] texture on to a basic curve for which the randomly oriented material is responsible. The size of the secondary maxima can readily be interpreted in terms of the gradual increase in strength of the [111] texture as the temperature of annealing is increased.

Similarly, in Fig. 16, the difference between the 400°

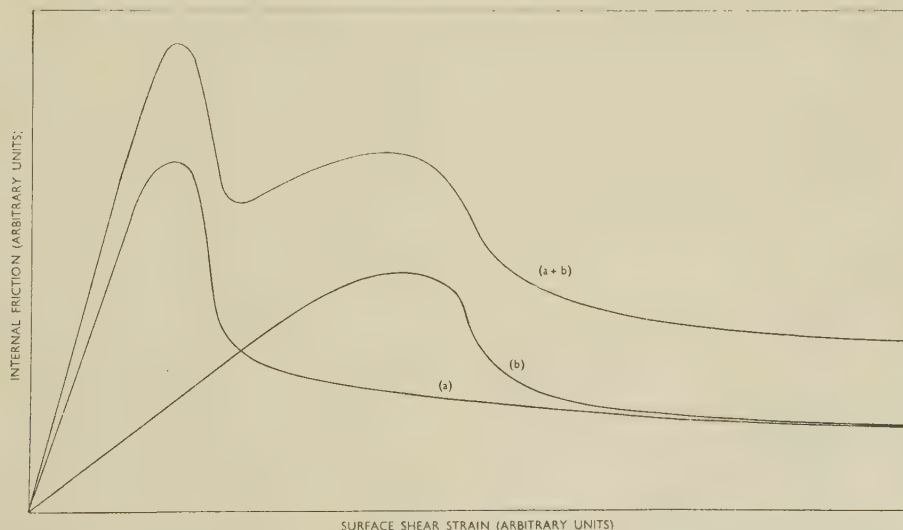


FIG. 25.—Diagrammatic Representation of the Manner in Which the Application of an Increasing Degree of Strain to a Polycrystalline Specimen Having Two Distinct Orientations Results in an Internal-Friction Curve Exhibiting Both Primary and Secondary Maxima.

and 600° C. curves can be explained by the proportional increase in number of grains having a [111] alignment as the annealing temperature is increased.

It can be seen from the geometry of the construction illustrated in Fig. 25 that the width of any maximum caused by a preferred orientation will be proportional to the external strain at which it occurs. This prediction is confirmed by the shape of the experimental curves.

## 2. THE RECOVERY PROCESS

The internal-friction curves (Figs. 5, 14, and 18) demonstrate very forcibly that the behaviour of high-purity copper during recovery from the effects of plastic deformation differs considerably from that of commercially pure material. An essential feature is the confirmation they afford that the changes of internal friction which occur at room temperature after the application of strain are not directly related to the accompanying changes of elastic modulus. Comparison of the internal-friction curves with the frequency curves reproduced in Figs. 6, 15, and 19, shows that the elastic modulus invariably increases with time after straining, whereas the internal friction might either increase or decrease. Similarly, the results on tough-pitch copper showed that the proportional changes of internal friction which occurred in a given time after the application of strain were independent of any factor except the magnitude of the strain increment causing them, whereas the corresponding changes of elastic modulus depended also upon the temperature at which the specimen had originally been annealed.

Since both the tough-pitch and the high-purity copper recovered their elastic moduli in a similar manner after straining, it seems probable that the recovery mechanisms for internal friction and frequency are distinct, and that only the one resulting in a change of decrement with time after straining is purity-sensitive.

Nowick<sup>22</sup> has suggested that the decrease of decrement at room temperature may be due to an interaction between dislocations and impurity atoms. In view of the low activation energies associated with the recovery process, he concluded that the mechanism was more likely to be one involving a migration of dislocations to impurity atoms than the reverse. Such a mechanism would result in effects different from those produced by strain-ageing in iron, for example, because the mobility of the dislocations would decrease as the degree of strain increased. It is conceivable that the recovery process occurring at high total strains may be largely due to an interaction between dislocations and that the impurity-locking mechanism is of secondary importance at this end of the strain range.

The existence of these two mechanisms working in conjunction could explain the observed sensitivity to small strain increments and the fact that the changes in internal friction become virtually independent of the magnitude of the strain increment when this is large.

The behaviour of the high-purity samples is not readily explained. A rise of internal friction with time after straining is difficult to interpret in terms of an impurity-locking hypothesis. In the theory of strain-ageing due to Cottrell,<sup>27</sup> solute atoms become mobile under the action of random thermal fluctuations and are acted upon by the stress field of edge dislocations. Under

these conditions, they congregate on those sites which permit them to relieve the hydrostatic component of the dislocation stress field. The segregation produced by such a process results in a reduction of the strain energy of the system as a whole and is therefore an equilibrium condition.

A mobile dislocation, however, will endeavour to pass through as many fixed impurity atoms as possible, though it will at the same time avoid increasing its length unduly. In the case of moderately pure materials, so many interactions occur per unit length of dislocation that the resultant decrease in the volumetric strain energy far outweighs the slight energy increment caused by the increased line-tension component. Under these conditions, a rapid decrease of internal friction after straining is to be expected.

In materials of very high purity, however, it is possible that a dislocation may have to move a considerable distance to interact with only a few impurity atoms, and that under these conditions the increased line-tension component would become comparable in magnitude to the strain-energy relief caused by impurity interaction. The impurity-locking mechanism might therefore become inoperative, and more stable internal conditions be achieved by the operation of a mechanism which need not necessarily result in a reduction of decrement with time after straining. Such a process might, in fact, result in effects similar to those observed with the high-purity sample originally annealed at 400° C.

The different behaviour of the specimen annealed at 600° C. can perhaps be explained by the tendency of impurity atoms to segregate round grain boundaries. Thomas and Chalmers<sup>28</sup> have demonstrated that this impurity concentration round grain boundaries varies inversely with annealing temperature. After annealing at 400° C., it is possible that enough of the impurities segregated to the grain boundaries to leave the centre of the grains sufficiently pure to prevent operation of the impurity-locking mechanism, thus leading to an increase of decrement with time after the application of strain. After annealing at 600° C., however, sufficient impurities remained to permit interaction to occur, thus leading to an internal friction which decreased slowly with time after the application of strain.

The discussion has so far been confined to the conditions prevailing in comparatively lightly strained material. The mechanism postulated is not expected to operate when the dislocation density is high. An examination of the curves shown in Fig. 14 discloses a gradual transition between the rising trend corresponding to the lower strains and the descending curves at the high-strain end. These descending curves are believed to be due to interaction between dislocations, with the consequent formation of some type of domain structure.

No completely satisfactory explanation can be advanced for the initial rapid increase of decrement observed at the high-strain end of the programme to which the high-purity specimen annealed at 600° C. had been subjected. Micro-examination of the control sample of this specimen disclosed that recrystallization had proceeded to a much higher degree than it had in the specimen annealed at 400° C. Conditions favourable to the occurrence of fine slip would occur preferentially in this sample. It is tempting, therefore, to suggest analogies between this phenomenon and the work-



softening effect originally observed by Brown,<sup>29</sup> and later discussed by Nabarro,<sup>30</sup> which depends upon the existence of fine slip.

### 3. STRAIN, INTERNAL FRICTION, AND ELASTIC MODULUS

The results have shown that an increasing shear strain progressively reduces the modulus of rigidity. No rising trend has been observed for strains up to 0.3 radian. Since the internal friction decreased rapidly when a critical shear strain had been exceeded, it is obvious that no unique relationship exists between internal friction and elastic modulus. The two factors must be related to some extent, however, because conditions of high internal friction were invariably found to coincide with local minima on the elastic-modulus curves.

The view might be taken that the permanent decrease of elastic modulus is due to the introduction of relatively mobile dislocations by plastic deformation.<sup>23-25</sup> Whereas the internal-friction effects depend presumably upon the thermally activated or virtually instantaneous movement of dislocations under the action of stress, a reduction of elastic modulus need involve only their vibration about some mean position. This hypothesis accounts for the fact that a considerable increase in the amplitude of vibration of strained material increases the decrement<sup>1,2</sup> without altering the elastic modulus appreciably.<sup>26</sup>

It is possible that, in the early stages of straining, dislocations responsible for the decrease of elastic modulus also contribute towards the internal friction. As the degree of strain increases, however, these dislocations, although still free to vibrate, will find it increasingly difficult to break away from locking points. They will therefore be able to contribute towards the decrease of rigidity long after they have ceased effectively to dissipate vibrational energy.

The fact that the room-temperature recovery of rigidity is not purity-sensitive makes it convenient to accept Smith's hypothesis<sup>26</sup> that this process is associated with the behaviour of screw dislocations. In confirmation of the present results, Smith found that both O.F.H.C. and spectroscopically pure copper recovered their elastic coefficients in the same manner at room and at slightly elevated temperatures. He attributed the recovery process to the behaviour of dislocation loops in different planes. When the screw component of one loop lies above, and parallel with, the screw

component of opposite sign of the other, thermal energy allows the two to unite to form a single loop joined by two short edge dislocations.

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# 1780 EQUILIBRIUM CONDITIONS IN THE COPPER-OXYGEN-CADMIUM-PHOSPHORUS SYSTEM \*

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(Communication from The British Non-Ferrous Metals Research Association)

## SYNOPSIS

The results are described of a series of slag/metal fusions in which copper containing small amounts of phosphorus and cadmium was brought into equilibrium at 1200° C. with a copper-oxygen-cadmium-phosphorus slag. A further series of fusions were made with cadmium-free metal and slag. Analysis of the metal phase showed that the concentrations of oxygen [O] and phosphorus [P] are related by :

$$[P][O]^2 = \text{constant} = 2.9 \times 10^{-7} \text{ wt.-%}$$

in the cadmium-free system, and by :

$$[P][O]^6 = \text{constant} = 1.3 \times 10^{-16} \text{ wt.-%}$$

in the cadmium-containing system.

The slags produced had the general formulæ  $x\text{Cu}_2\text{O} \cdot y\text{P}_2\text{O}_5$  (cadmium-free system) and  $(x-z)\text{Cu}_2\text{O} \cdot z\text{CdO} \cdot y\text{P}_2\text{O}_5$  (cadmium-containing system), cadmium oxide replacing cuprous oxide approximately molecule for molecule in the cadmium-containing system.

The bearing of these equilibrium studies on deoxidation practice in the commercial manufacture of copper-cadmium wire-bars is discussed in detail. Fortuitously, the equilibrium oxygen and phosphorus contents of phosphorus-deoxidized copper-cadmium alloys are similar to those obtaining in cadmium-free alloys in the range of compositions of commercial interest (0.003-0.03% phosphorus), although outside these limits they differ considerably. The composition of the deoxidation product (slag) shows that in both cadmium-free and cadmium-containing alloys, deoxidation with 1 unit by weight of phosphorus removes about 1.8 units of oxygen. A theoretical interpretation of the results in terms of the ionic theory of slags is suggested in an Appendix.

## I.—INTRODUCTION AND SUMMARY

THE work described in this report forms part of a study of cracking and other difficulties found in the commercial production of wire-bars in copper-cadmium alloys, and described in detail elsewhere.<sup>1-3</sup> A probably important factor in any such research is the extent to which the product is unsound, and, in fact, previous investigations<sup>1-3</sup> have shown that considerable unsoundness frequently occurs in such wire-bars. This unsoundness was thought to be due, among other causes, to inadequate deoxidation of the metal before casting. A particular difficulty arises in the deoxidation of this alloy owing to the necessity for ensuring a high electrical conductivity in the wire finally produced. Deoxidation is normally achieved by adding phosphorus to the alloy, and although the product of the deoxidation reaction has little effect, any residual unreacted phosphorus markedly lowers the conductivity; it is therefore important that the amount of phosphorus added be the minimum necessary to effect adequate deoxidation, bearing in mind that a small amount of residual phosphorus is required to buffer the oxygen dissolved in the residual liquid during freezing.

The information needed for computation of the

minimum deoxidizing addition and minimum residual phosphorus content is: (a) the composition of the deoxidation product, which governs the amount of oxygen removed by a given phosphorus addition; (b) the oxygen content to be removed by deoxidation; and (c) a knowledge of the equilibria between the phosphorus and oxygen contents of the metal and the slag composition, which permits determination of the necessary residual phosphorus content, and of the effect of the deoxidation treatment on the equilibrium between steam and the molten alloy. Information on (a) and (c) is available for pure copper from the work of Baker,<sup>4</sup> who showed that, for melts whose phosphorus content falls in the range 0.003-0.03%, the deoxidation product has the approximate composition  $2\text{Cu}_2\text{O} \cdot \text{P}_2\text{O}_5$ , 1 unit by weight of phosphorus therefore removing about 1.8 units of oxygen. In addition, Baker found that the equilibrium between the phosphorus and oxygen contents of the metal is given by:

$$\text{Log } [P][O]^{2.5} = 0.01177T - 25.18$$

where  $T$  is the temperature in °K.

As it was not known whether Baker's work was applicable to copper containing up to about 1% cadmium, the work reported here was carried out to determine the

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effect of cadmium on the equilibrium concentrations of oxygen and phosphorus in molten copper at 1200° C. It was hoped that the data obtained, together with other work<sup>2,5</sup> on the pick-up of oxygen and hydrogen during the melting of the alloy, would enable sound wire-bars to be made consistently in industrial practice.

Briefly, the procedure employed in the present investigation was to melt a copper-cadmium alloy in contact with copper-cadmium phosphate slags of various compositions in a closed silica vessel, hold the slag and metal charge at 1200° C. for 30 min., cool rapidly, and analyse the resulting materials. The use of a closed silica vessel was necessary to prevent loss of cadmium from the system owing to its high vapour pressure.

Some slag/metal fusions of phosphorus-deoxidized copper and cadmium-free copper phosphate slags of various compositions were made, so that a comparison of the results of the present work could be made with those of Baker.<sup>4</sup> These check experiments were in good agreement, thus showing that the minor differences in technique had little significant effect.

Over the range 0.001–0.1% phosphorus, the relationship between the oxygen and phosphorus contents of molten copper at 1200° C. was found to be:

$$[P][O]^2 \simeq 2.9 \times 10^{-7} \text{ wt.-%} \quad (1)$$

(As discussed later, this relationship differs slightly from that found by Baker.) The corresponding relationship for cadmium-bearing alloys was found to be:

$$[P][O]^6 \simeq 1.3 \times 10^{-16} \text{ wt.-%} \quad (2)$$

The difference between relationships (1) and (2) indicates that the presence of cadmium considerably affects the activities of the various components of the system. However, the lines representing the relationship between the oxygen and phosphorus contents of copper melts, with and without cadmium, cross at about 0.01% phosphorus (Fig. 6, p. 511).

Since this composition lies in the middle of the range of practical interest (0.003–0.03% phosphorus), the difference, at a given phosphorus content within the range, between the oxygen contents of cadmium-bearing and cadmium-free alloys is small. Furthermore, cadmium oxide appears to replace cuprous oxide in the slag nearly molecule for molecule, so that the presence of cadmium does not significantly affect the ratio of phosphorus to oxygen in the slag separating from the melt. Consequently, the amount of phosphorus necessary for adequate deoxidation of a copper melt is hardly affected by the presence of cadmium, and it is shown that, as with a melt of pure copper, 1 unit by weight of phosphorus removes about 1.8 units of oxygen from a copper-cadmium melt.

The relationship obtained for the equilibrium between the phosphorus and oxygen contents of copper-cadmium melts at 1200° C., enables the minimum residual phosphorus content after deoxidation to be estimated as about 0.004% (the exact value depends on the hydrogen content of the melt), and information on the oxygen pick-up by these melts obtained elsewhere<sup>2,5</sup> indicates that, in normal commercial practice, adequate deoxidation should be secured by a phosphorus addition of 0.008%.

The theoretical aspects of the equilibria studied are discussed in an Appendix (p. 512).

## II.—EXPERIMENTAL

### 1. MATERIALS

The materials used in making up the charges for the equilibrium studies were prepared in the laboratory as stated below.

#### (a) Metals

Cathode copper was melted under a layer of charcoal in a covered, alumina-coated Salamander crucible and heated to 1300° C. in a gas-fired furnace. The metal was purged with "white-spot" nitrogen and deoxidized with 0.03% phosphorus (as a copper-15% phosphorus hardener). Cadmium, as a 50% cadmium-copper hardener, was stirred in and the metal cast at about 1230° C. into a 2-in.-dia. copper mould by means of an alumina-coated tundish. A similar procedure was followed in making metal free from cadmium.

The resulting ingots were machined to remove surface irregularities, and cut longitudinally into strips of approximately 1 cm. square cross-section for subsequent slag/metal fusions. Analyses of these materials and of the cathode copper are given in Table I.

#### (b) Slags

Copper-cadmium phosphate and copper phosphate slags were made by melting together suitable proportions of cuprous oxide, cadmium oxide, and phosphorus pentoxide in a copper crucible with a close-fitting lid.

The crucible was heated in a gas-fired furnace and a stream of nitrogen directed over the charge during melting and casting. The slags were cast into a copper mould, crushed, and ground.

Analyses of materials used in making the slags are given in Table I.

### 2. SLAG/METAL FUSIONS

The apparatus used is shown diagrammatically in Fig. 1. About 30 g. of the metal and 8 g. of a suitable mixture of pre-fused slag powders were charged into a conical recrystallized alumina crucible. The crucible and its contents were then sealed into a silica tube welded to a long capillary tube, also of silica, as shown in Fig. 1; sealing was carried out by using a ring of oxygen-hydrogen jets. This assembly was lowered into a vertically mounted platinum-wound furnace controlled at 1200° C., and any moisture in the system was allowed to boil out. When the moisture had been removed, a silica stopper rod was placed in the capillary tube, and the open end closed with a Bunsen valve which prevented entry of air while allowing the internal atmosphere to expand.

The charge was allowed to attain 1200° C., checked by a platinum/platinum-rhodium thermocouple placed alongside the silica tube as shown in Fig. 1, and held at this temperature for 30 min. (Check tests with a holding time of 60 min. were carried out to ensure that equilibrium had been attained in the 30-min. tests.)

The assembly was then withdrawn from the furnace and rapidly cooled to about 800° C. in an air blast from a ring of jets, and finally cooled to room temperature by immersion in water. After cooling, the alumina crucible was removed from the silica tube and broken away from its contents.

The contents of the crucibles consisted of metal buttons about 1½ in. long with slag adhering to the tops and sides. As much as possible of the slag was carefully broken away from each button, crushed, ground, and

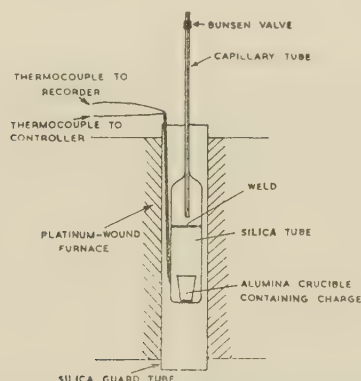


FIG. 1.—Apparatus Used in Slag/Metal Fusion.

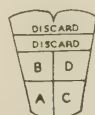


FIG. 2.—Section of Metal Buttons, Showing Analytical Samples Marked A, B, C, and D.

analysed. The remaining slag adhering to the sides of the metal button was chipped and filed away, and the button was sectioned longitudinally and examined under the microscope for piping and slag inclusions. The

TABLE I.—*Analyses of Materials Used in Equilibrium Studies (Per Cent.).*

	Cathode Copper	Cu-1% Cd Alloy	P.D.O. Copper	Cadmium Oxide	Cuprous Oxide
Antimony . . .	<0.0002	<0.0002	<0.0002	<0.0002	0.0008
Arsenic . . .	<0.001	<0.001	<0.001	<0.001	0.002
Bismuth . . .	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Cobalt . . .	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Iron . . .	<0.0002	0.0005	<0.0002	<0.0002	0.003
Lead . . .	~0.0001	0.0005	0.0004	<0.01	0.003
Phosphorus . .	<0.005	0.025 *	0.0042 *	<0.001	<0.005
Silicon . . .	<0.001	~0.001	<0.001	<0.001	0.01
Manganese . .	<0.001	0.001	0.001	<0.001	<0.001
Nickel . . .	<0.0001	0.0003	0.0003	<0.0003	0.001
Silver . . .	~0.001	0.002	0.002	<0.002	0.002
Tin . . .	<0.005	0.0005	0.0005	<0.0005	<0.0005
Zinc . . .	<0.001	<0.001	<0.001	<0.01	<0.001
Tellurium . .	<0.001	<0.001	<0.001	<0.001	<0.001
Cadmium . . .	...	0.96 *	...	87.52 *	...
Copper . . .	Bal.	Bal.	Bal.	Mg <0.01	87.38 *

\* Chemical analyses; remainder spectrographic analyses.

sections containing the pipe and inclusions and the sections immediately below were discarded and the remainder of the buttons were sectioned, as shown in Fig. 2, and analysed.

### 3. ANALYSES

#### (a) Oxygen

The normal B.N.F.M.R.A. method for the determination of oxygen in copper by hydrogen reduction was believed to be unsatisfactory with copper-cadmium alloys; cadmium vapour was expected to interfere, since the water vapour formed in the reaction would be in contact with warm condensed cadmium films for a considerable period and might be partially decomposed. The oxygen content of the samples was therefore determined by vacuum fusion in a carbon crucible. This method avoids the difficulties mentioned, since the oxygen is converted to carbon monoxide, which is rapidly pumped away from the hot zone. The results are thought to be satisfactory because, in every run, treatment of several copper-cadmium samples in the same crucible was followed by a treatment of a copper-oxygen alloy of known oxygen content and the latter sample gave the expected result.

#### (b) Copper

Copper was determined electrolytically from a sulphuric/nitric acid solution.

#### (c) Cadmium

Cadmium was determined by a method developed by the B.N.F.M.R.A. The sample was dissolved in a mixture of nitric and hydrochloric acids, the copper precipitated as oxalate, and the cadmium determined polarographically. The results of the determination are considered to be accurate to  $\pm 3\%$ . Cadmium in the slags was determined electrolytically in sulphuric acid solution from which the copper had been removed.

#### (d) Phosphorus

Phosphorus was also determined by a B.N.F.M.R.A. method. This consisted of dissolving the sample in nitric acid and evaporating the solution to dryness to oxidize the phosphorus. The copper was removed in an ion-exchange column, and the phosphorus determined spectrophotometrically by means of the reduced phosphomolybdate colour.

#### (e) Aluminium

Aluminium in the slag was determined gravimetrically. The slag was dissolved in sulphuric acid, the copper and cadmium removed by mercury-cathode electrolysis, and the resulting solution passed through an ion-exchange column which retained the aluminium. The aluminium was removed by elution with hydrochloric acid, and precipitated as aluminium hydroxide, which was ignited and weighed as  $\text{Al}_2\text{O}_3$ .

## III.—RESULTS AND DISCUSSION

The results obtained from the fusions of cadmium-free and cadmium-containing materials are presented in Tables II and III, respectively, and are discussed separately below.



TABLE II.—Results of Slag/Metal Fusions: Copper-Oxygen-Phosphorus Alloys.

Melt No. RRQ	Slag Analysis			Metal Analysis		$[P][O]^2$ wt.-%
	Cu, %	P, %	Al, %	P, %	O, %	
17	47.8	18.3	1.7	0.080	0.0016	$2.0 \times 10^{-7}$
18	48.0	18.5	1.6	0.10	0.0017	$2.9 \times 10^{-7}$
19	48.4	18.2	1.3	0.084	0.0014	$1.7 \times 10^{-7}$
20	48.1	18.3	1.5	0.11	0.0012	$1.6 \times 10^{-7}$
22	49.2	18.3	1.4	0.029	0.0036	$3.8 \times 10^{-7}$
21	49.4	18.1	1.3	0.029	0.0018	$0.9 \times 10^{-7}$
23	49.8	18.0	1.4	0.021	0.005	$5.3 \times 10^{-7}$
24	49.4	18.3	1.4	0.025	0.0038	$3.2 \times 10^{-7}$
15	50.6	18.2	1.4	0.0053	0.0063	$1.4 \times 10^{-7}$
16	50.2	18.2	1.3	0.0035	0.011	$4.2 \times 10^{-7}$
13	53.6	17.0	1.3	0.0025	0.0061	$0.9 \times 10^{-7}$
14	53.7	16.9	1.3	0.0029	0.013	$4.9 \times 10^{-7}$
11	54.6	16.2	1.0	0.0003	0.021	$1.3 \times 10^{-7}$
12	54.6	16.3	0.9	0.0016	0.017	$4.6 \times 10^{-7}$
9	57.0	14.8	0.9	0.0015	0.011	$1.8 \times 10^{-7}$
10	56.4	15.5	1.1	0.0006	0.016	$1.8 \times 10^{-7}$
2	58.8	13.2	1.1	0.0007	0.029	$5.9 \times 10^{-7}$
3	58.6	13.3	1.1	0.0006	0.026	$4.1 \times 10^{-7}$
5	63.0	11.2	1.2	0.0002	0.16	$51 \times 10^{-7}$
6	62.9	11.4	1.2	0.0002	0.17	$58 \times 10^{-7}$
4	65.1	9.7	1.9	0.0007	0.36	$910 \times 10^{-7}$
7	65.4	9.8	1.8	<0.0001	0.42	$<170 \times 10^{-7}$
8	65.3	9.6	1.9	0.0002	0.41	$340 \times 10^{-7}$

logarithmic basis, the resultant points lie near a straight line \* having a slope of about 2.0. The product  $[P][O]^2$  is therefore approximately constant ( $2.9 \times 10^{-7}$  wt.-%) in this composition range, as shown by the last column in Table II. A slightly different relationship was found by Baker<sup>4</sup> in earlier work at 1200° C.:

$$[P][O]^{2.5} = \text{constant},$$

but the relationship quoted above, which was derived from the more numerous results of the present work, was unchanged by the inclusion of the results of Baker's<sup>4</sup> work, which fell within the same scatter band.

The copper contents of the slags are plotted against their phosphorus contents in Fig. 6 (p. 511), the alumina present being neglected and the copper and phosphorus contents being scaled up accordingly and expressed as moles of oxide/100 g. The plotted points fall on or about the line representing slags of the composition  $x\text{Cu}_2\text{O}.y\text{P}_2\text{O}_5$ , in agreement with the earlier work.<sup>4</sup>

TABLE III.—Results of Slag/Metal Fusions: Copper-Oxygen-Cadmium-Phosphorus Alloys.

Melt No. RRG	Slag Analysis				Metal Analysis			$[P][O]^2$ , wt.-%
	Cu, %	Cd, %	P, %	Al, %	Cd, %	P, %	O, %	
21	18.6	29.4	19.6	1.3	0.60	0.36	0.0031	$3.2 \times 10^{-16}$
22	18.6	30.1	19.4	1.4	0.69	0.41	0.0025	$1.0 \times 10^{-16}$
13	18.5	36.8	17.8	1.2	0.54	0.10	0.0030	$0.7 \times 10^{-16}$
12	15.2	35.3	17.5	1.2	0.49	0.11	0.0038	$3.3 \times 10^{-16}$
14	14.2	37.0	17.4	1.1	0.58	0.066	0.0025	$0.2 \times 10^{-16}$
15	13.9	36.2	17.4	1.0	0.61	0.062	0.0043	$3.9 \times 10^{-16}$
17	14.0	37.8	17.0	0.9	0.54	0.031	0.0040	$1.3 \times 10^{-16}$
18	14.1	37.9	17.0	1.0	0.52	0.042	0.0028	$0.2 \times 10^{-16}$
16	14.3	37.5	16.9	1.0	0.57	0.040	0.0044	$2.9 \times 10^{-16}$
30	14.0	39.8	16.4	0.6	0.64	0.034	0.0036	$0.7 \times 10^{-16}$
29	14.0	39.5	16.2	1.0	0.71	0.013	0.0029	$0.8 \times 10^{-16}$
28	12.2	42.5	15.8	0.8	0.85	0.033	0.0038	$1.0 \times 10^{-16}$
27	11.8	42.7	15.5	0.8	0.74	0.030	0.0042	$1.6 \times 10^{-16}$
3	18.3	34.8	16.3	0.8	0.51	0.036	0.0040	$1.5 \times 10^{-16}$
26	20.5	34.1	16.3	0.9	0.43	0.015	0.0042	$0.8 \times 10^{-16}$
25	20.6	34.2	16.0	0.8	0.37	0.013	0.0038	$0.4 \times 10^{-16}$
2	14.1	38.3	16.0	1.1	0.73	0.036	0.0040	$1.5 \times 10^{-16}$
24	11.1	44.2	15.9	1.1	0.78	0.022	0.0039	$0.8 \times 10^{-16}$
23	11.3	44.1	15.8	1.1	0.87	0.021	0.0047	$2.3 \times 10^{-16}$
19	17.6	37.3	15.6	0.9	0.42	0.0046	0.0037	$0.1 \times 10^{-16}$
20	17.7	37.6	15.5	1.1	0.41	0.0051	0.0044	$0.4 \times 10^{-16}$
7	17.2	39.9	15.0	0.7	0.41	0.0017	0.0060	$0.8 \times 10^{-16}$
4	16.7	40.3	14.7	0.6	0.37	0.0006	0.013	$29 \times 10^{-16}$
6	14.1	45.3	12.3	2.3	0.68	<0.0001	0.027	$<0.04 \times 10^{-16}$
9	14.5	45.1	12.2	2.5	0.62	0.0005	0.032	$0.54 \times 10^{-16}$
8	10.7	53.3	11.0	1.4	1.36	0.0006	0.27	$2.3 \times 10^{-10}$
5	10.2	53.8	10.8	1.4	1.28	0.0002	0.23	$3.0 \times 10^{-10}$
11*	10.5	53.7	10.8	1.6	1.25	<0.0001	0.27	$<3.9 \times 10^{-10}$
10*	10.7	52.9	10.4	1.8	1.30	<0.0001	0.23	$<1.5 \times 10^{-10}$

\* Held for 60 min. at 1200° C.; remainder held at temperature for 30 min. only.

### 1. CADMIUM-FREE ALLOYS

The oxygen and phosphorus contents of the cadmium-free alloys are plotted on logarithmic scales against each other in Fig. 3, together with the results obtained by Baker.<sup>4</sup> The close agreement between the two series of points indicates that the slight differences in experimental techniques had little or no effect.

Fig. 3 shows that when the oxygen contents of alloys with a phosphorus content within the range 0.001–0.1% are plotted against the phosphorus contents on a

### 2. CADMIUM-BEARING ALLOYS

In the slag/metal fusions of cadmium-bearing materials, the initial cadmium content of the metal used was 0.96%; the final cadmium content depended on the slag composition, particularly the ratio of cadmium to copper. As this relationship was not known at the beginning of the work, it was necessary to guess the composition of the initial slag charges, and on this account there was a transfer of cadmium (as well as oxygen and phosphorus) between the slag and the metal (see especially Melts 8, 5, 11, and 10 in Table III), the final cadmium contents of most of the buttons being within the range 0.4–0.8%. However, this variation in cadmium content did not appear to affect greatly the relationship between the oxygen and phosphorus content of the buttons.

The relationship between the concentrations of oxygen and phosphorus at 1200° C. in copper-cadmium alloys can also be represented on a logarithmic plot by a straight line, as shown in Fig. 4. This line has a slope of approximately 6.0, so that the product  $[P][O]^6$  is constant ( $1.3 \times 10^{-16}$  wt.-%) over the range from 0.5 to 0.001% phosphorus, as indicated by the last column of Table III.

To facilitate comparison with the cadmium-free alloys, the lines obtained from the logarithmic plots of Figs. 3 and 4 have been re-plotted in the same diagram in Fig. 5. Over the range of phosphorus contents of practical interest for deoxidation, namely 0.003–0.03%, the effect of the added cadmium is slight, and inspection of Fig. 6 shows that the lines representing the equilibrium between the oxygen and phosphorus contents of the alloys cross at about 0.01% phosphorus and 0.004% oxygen. Equilibrium at only one temperature was investigated in the present work, but the above finding suggests that Baker's results<sup>4</sup> for equilibrium at other temperatures should be applicable to copper-cadmium alloys without large error.

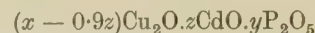
It was shown in the preceding section that the com-

\* The lines shown in Figs. 3 and 4 are the best lines obtainable from the experimental points and have been derived statistically by the method of least squares. Alloys containing less than

0.0005% phosphorus have not been included in the statistical calculations, owing to the low accuracy of the phosphorus determination at these small concentrations.

position of the cadmium-free slags can be represented by the general formula  $x\text{Cu}_2\text{O} \cdot y\text{P}_2\text{O}_5$ . To determine the corresponding formula of the cadmium-containing slags, the sum of their  $\text{Cu}_2\text{O}$  and  $\text{CdO}$  contents, expressed in moles/100 g., was plotted against the  $\text{P}_2\text{O}_5$  content (Fig. 6). The line obtained from this plot almost

that for the latter slags corresponds more exactly to the general composition:



in which every nine  $\text{Cu}_2\text{O}$  molecules are replaced by ten  $\text{CdO}$  molecules.

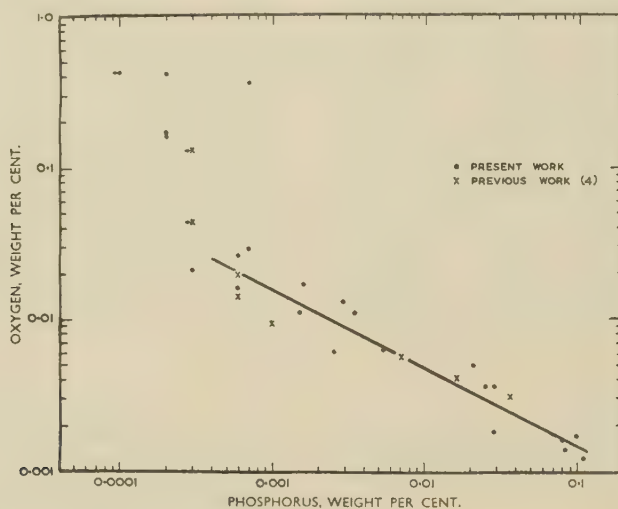


FIG. 3.—Relationship Between the Equilibrium Oxygen and Phosphorus Contents of Molten Copper at 1200° C.

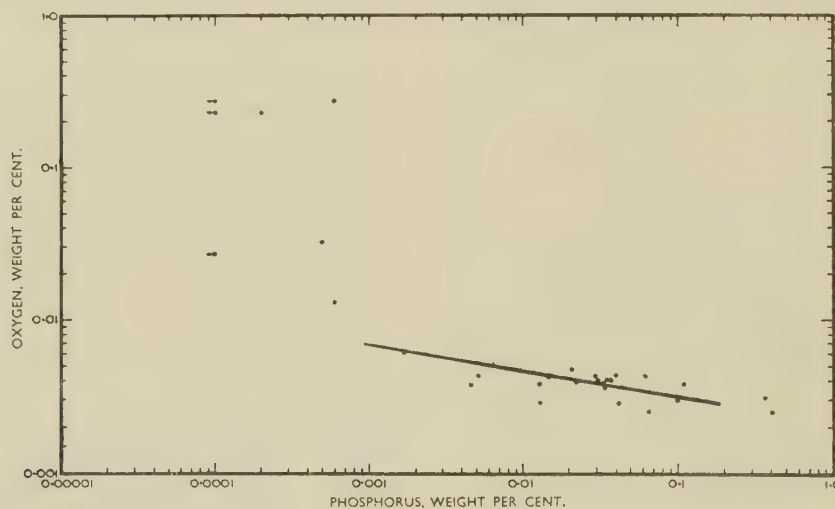
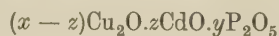


FIG. 4.—Relationship Between the Equilibrium Oxygen and Phosphorus Contents of Copper-1% Cadmium Alloys at 1200° C.

coincides with the similar plot of the  $\text{Cu}_2\text{O}$  contents of the cadmium-free slags, thus indicating that  $\text{CdO}$  substitutes for  $\text{Cu}_2\text{O}$  on an approximately molar basis; \* i.e. that the slag composition may be approximately represented by the general formula:



If the difference between the lines for the cadmium-free and cadmium-containing slags in Fig. 6 is significant,

It follows that the presence of cadmium does not significantly affect the ratio of phosphorus to oxygen in the slag, since cadmium oxide replaces cuprous oxide almost molecule for molecule. Hence, the amount of phosphorus necessary for adequate deoxidation at 1200° C. of copper-cadmium melts of given oxygen content is not appreciably different from that required to treat a cadmium-free melt of the same oxygen content. Copper-cadmium alloys commonly contain 0.003–0.03%

\* This argument tacitly makes the reasonable assumption that the densities of liquid copper-oxygen-phosphorus and copper-oxygen-cadmium-phosphorus slags are not significantly different.



phosphorus after deoxidation, and a plot of the distribution of phosphorus between the metal and the slag at 1200° C. proves that this range corresponds to slags containing 15–17% phosphorus. It can be shown with

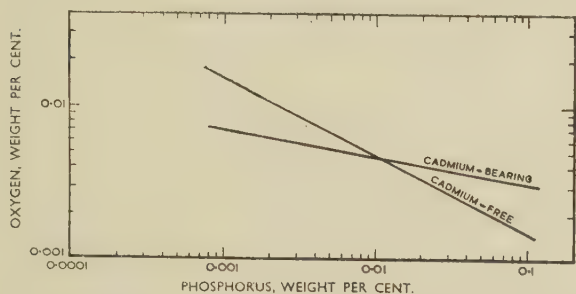


Fig. 5.—Effect of Cadmium on the Relationship Between the Equilibrium Oxygen and Phosphorus Contents of Molten Copper at 1200° C.

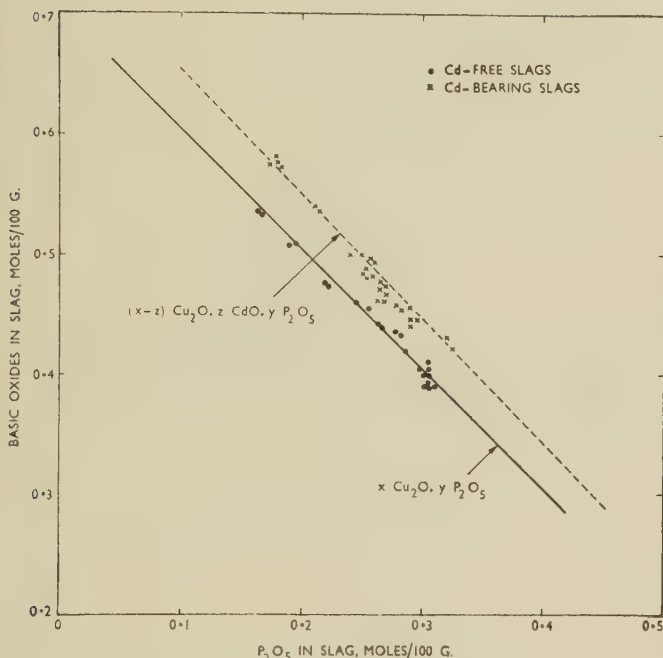


Fig. 6.—Composition of Slags After Fusion.

the aid of Fig. 6 that slags in the middle of this range have the approximate composition :



Hence 1 unit by weight of phosphorus removes about 1.8 units by weight of oxygen from a copper-cadmium melt at 1200° C. This figure is identical with the value found by Baker<sup>4</sup> for the deoxidation of cadmium-free metal at the same temperature, for the same range of phosphorus contents.

The slag composition and the plot of the equilibrium contents of phosphorus and oxygen in the metal (Fig. 4) enable a further important deduction to be made. When

an adequate deoxidizing addition of phosphorus is made to a melt which contains more than enough oxygen to reach equilibrium with the addition, some of the oxygen is immediately precipitated as a phosphate slag which rises rapidly to the surface.<sup>4</sup> Further precipitation of slag takes place during subsequent cooling and freezing and, as Baker has shown for pure copper,<sup>4</sup> this results in the removal from solution of nearly all the residual oxygen, together with any picked up during pouring, leaving a small excess of phosphorus during freezing; most of the slag precipitated at this stage is trapped in the casting, so that analyses of the solid metal are representative of the phosphorus and oxygen in solution

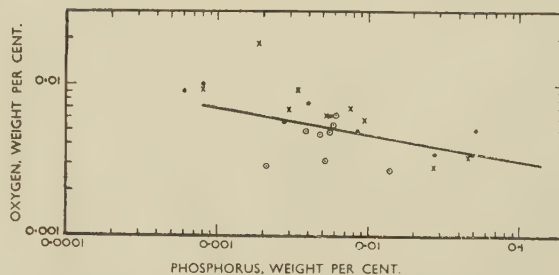


Fig. 7.—Relationship Between the Oxygen and Phosphorus Contents of Industrial and Laboratory Melts.

KEY		Casting Temp.
x	Gassed laboratory melts	1200°–1250° C.
•	Purged	
○	Industrial melts	1150°–1200° C.

The line represents the equilibrium between the oxygen and phosphorus contents of cadmium-containing alloys at 1200° C.

just before pouring. If, on the other hand, the phosphorus addition is too small, all the phosphorus remaining in solution after the deoxidizing addition has been made will be precipitated as slag during solidification, and an excess of oxygen will remain which can then segregate in the residual liquid and give rise to the steam reaction, if enough hydrogen is present.

The slag analyses quoted above indicate that 1 unit by weight of phosphorus removes about 1.8 units of oxygen as phosphate slag at 1200° C., and the proportions are probably similar in slags formed at lower temperature, as in cadmium-free alloys.<sup>4</sup> Consequently, if an excess of phosphorus is to remain in solution during freezing, the phosphorus necessary for deoxidation must be at least 0.53 times the residual oxygen plus any oxygen picked up during casting.\* In practice, this critical phosphorus content varies slightly with the concentration of hydrogen in the melt, for it has been found that if the hydrogen content is high, a small excess of phosphorus (about 0.002%) above the critical value is necessary to prevent unsoundness in the casting.<sup>5</sup>

If strongly reducing conditions are continuously maintained during melting and casting, the oxygen pick-up may be so small that the critical residual phosphorus content may be as little as 0.002%.<sup>5</sup> Under normal conditions, however, even if the melt is prepared under a charcoal cover, the oxygen content rises to much higher values during casting. This is shown in Fig. 7, in which the residual oxygen contents of a number of experimental and production wire-bars prepared under

\* This simplified argument neglects the small traces of phosphorus and oxygen which remain in solid solution in equilibrium with the precipitated slag.

a variety of conditions are plotted against the residual phosphorus contents; the line (from Fig. 4) representing the equilibrium contents at 1200° C.—a normal temperature for deoxidation and casting—is included for comparison. The compositions of the castings fall near the equilibrium values within the same scatter band as obtained in Fig. 4,\* indicating that the oxygen contents of the alloys, whatever their initial values, rose during casting until they reached equilibrium with the residual phosphorus at the pouring temperature. The reasons why the equilibrium contents were attained but not significantly exceeded in pouring, are discussed elsewhere;<sup>5</sup> the important deduction from this observation is that, in alloys cast under any but strongly reducing conditions, the critical residual phosphorus content must be about 0.004%, because it is at this value that the equilibrium oxygen content is 1.8 times as great (0.006%). This critical value agrees well with that found in foundry experiments and under industrial conditions.<sup>2, 5</sup>

The addition of phosphorus required for deoxidation may be larger than the critical residual value of 0.004%, because some phosphorus may separate as slag before the alloy is poured; this latter quantity depends upon the oxygen content of the melt before deoxidation. No very accurate information exists with regard to the oxygen contents of copper-cadmium melts immediately before deoxidation, and in any case these contents appear to vary from one manufacturer to another,<sup>2</sup> presumably because deoxidation by a carbon cover is slow and the time of contact is variable. However, with good melting and casting practice, it seems that the oxygen content to be removed by deoxidation should not exceed 0.01%,<sup>2, 5</sup> in which event a deoxidizing addition of 0.008% phosphorus should leave a residual content of 0.006% (i.e. 0.002% more than the critical value), which should suffice to prevent unsoundness even if the melt contains much hydrogen.

#### ACKNOWLEDGEMENTS

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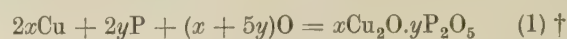
#### APPENDIX

##### THEORETICAL TREATMENT OF RESULTS

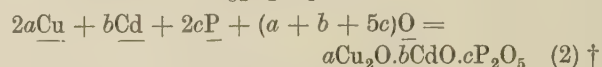
##### 1. MOLECULAR TREATMENT

In most theoretical treatments of the results of slag/metal equilibria, the reactants and products formed are represented by molecular formulæ such as FeO, SiO<sub>2</sub>, Cu<sub>2</sub>O, &c. On this basis, the reactions occurring in the

two systems studied in the present work might be represented by equations such as the following:



$$K_1 = \frac{a_{(x\text{Cu}_2\text{O} \cdot y\text{P}_2\text{O}_5)}}{a_{\text{Cu}}^{2x} \cdot a_{\text{P}}^{2y} \cdot a_{\text{O}}^{(x+5y)}}$$



$$K_2 = \frac{a_{(a\text{Cu}_2\text{O} \cdot b\text{CdO} \cdot c\text{P}_2\text{O}_5)}}{a_{\text{Cu}}^{2a} \cdot a_{\text{Cd}}^b \cdot a_{\text{P}}^{2c} \cdot a_{\text{O}}^{(a+b+5c)}}$$

In these equations, the symbols  $a_{\text{Cu}}$ ,  $a_{\text{P}}$ , &c., represent the activities of copper, phosphorus, &c. Some simplification of the above expressions for the equilibrium constants  $K_1$  and  $K_2$  is possible. In the first place the activity of copper is substantially unity in these systems, so that the terms containing  $a_{\text{Cu}}$  may be omitted. The terms containing  $a_{\text{Cd}}$  may also be omitted, since the activity of cadmium was held very approximately constant throughout the experiments.

Secondly, in view of the very low dilutions involved, it is a reasonable assumption that  $a_{\text{P}}$  and  $a_{\text{O}}$  obey Henry's law, i.e. that these activities are proportional to the corresponding mole fractions of the elements. It follows from these assumptions that:

$$K_1' = \frac{a_{(x\text{Cu}_2\text{O} \cdot y\text{P}_2\text{O}_5)}}{[\text{P}]^{2y}[\text{O}]^{(x+5y)}} \quad \dots \quad (3)$$

$$K_2' = \frac{a_{(a\text{Cu}_2\text{O} \cdot b\text{CdO} \cdot c\text{P}_2\text{O}_5)}}{[\text{P}]^{2c}[\text{O}]^{(a+b+5c)}} \quad \dots \quad (4)$$

If it could be further assumed that over the range of compositions studied in the present work the slag was of essentially constant composition and activity, the above equilibrium constants would become:

$$K_1'' = \frac{1}{[\text{P}]^{2y}[\text{O}]^{(x+5y)}} \quad \text{or} \quad [\text{P}][\text{O}]^{(x+5y)/2y} = \text{const.} \quad \dots \quad (5)$$

and

$$K_2'' = \frac{1}{[\text{P}]^{2c}[\text{O}]^{(a+b+5c)}} \quad \text{or} \quad [\text{P}][\text{O}]^{(a+b+5c)/2c} = \text{const.} \quad \dots \quad (6)$$

In this event, the relation between the phosphorus and oxygen contents of the metal phase would depend upon the composition of the slag. Thus, if in the copper-oxygen-phosphorus system, the slag was assumed to consist only of P<sub>2</sub>O<sub>5</sub> ( $x = 0$ ,  $y = 1$ ), the expected relation between [P] and [O] would be:

$$[\text{P}][\text{O}]^{2.5} = \text{const.} \quad \dots \quad (7)$$

Similarly, if the composition 3Cu<sub>2</sub>O.2P<sub>2</sub>O<sub>5</sub> be assumed for the slag, [P] and [O] would be related by:

$$[\text{P}][\text{O}]^{3.25} = \text{const.} \quad \dots \quad (8)$$

\* The scatter of the points in Fig. 7 may be partly the result of variable casting temperatures. There is a tendency for points corresponding to melts cast at temperatures above 1200° C. to fall above the 1200° C. equilibrium line; similarly, points corre-

sponding to melts cast below 1200° C. mainly fall below this line.

† The underlined symbols indicate that the substances concerned are dissolved in the metal phase.



Other relations can be derived in a similar way by assuming other slag compositions, the exponent of  $[O]$  increasing with increase in the  $Cu_2O$  content of the slag. Similar relations may be derived for the copper-oxygen-cadmium-phosphorus system, e.g. if the slag is assumed to have the composition  $Cu_2O.CdO.P_2O_5$ , there is obtained:

$$[P][O]^{3.5} = \text{const.} \quad . \quad . \quad . \quad (9)$$

Now, as shown in Tables II and III, the compositions of the slags in both the systems in fact vary considerably over the range studied, and on the above basis it is therefore surprising that a relation of the kind  $[P][O]^2 = \text{const.}$  should exist at all. Presumably this relationship exists because the change in the composition of the slag is cancelled out in the equilibrium constants by compensating changes in the activities of the slag components. The slag is a concentrated solution in which the activities of the components are unlikely to be proportional to their mole fractions.

Indeed, the departure from ideality of the activities in the slags must be considerable, because in the experimentally observed relation for the copper-oxygen-phosphorus system,  $[P][O]^2 = \text{const.}$ , the exponent of  $[O]$  is lower than the limiting value of 2.5 predicted by the above simple theory. Furthermore, the addition of cadmium causes the exponent of  $[O]$  to jump from 2 to about 6, and this surprising effect can be explained only by marked changes in the activities of the reactants.

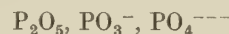
These departures from ideal behaviour of the assumed slag components mean that no simple relationships can be expected between the slag and metal phase compositions, in any approach of this kind in which the substances taking part in the reactions are represented by molecular formulæ. As most liquid slags are now held to consist of mixtures of ions rather than molecules, an attempt was made to derive some simple relationships between the metal and slag composition by representing the slag composition in terms of ions instead of molecules, it being reasoned that a treatment more in accord with the physical nature of the slags might meet with better success.

## 2. IONIC TREATMENT

According to the ionic theory, liquid slags are composed mainly of ions rather than molecules, so that in reactions with other phases the reacting species are generally ions, instead of molecules as assumed in the treatment given above. If the right model and ionic species are selected, the activities of the ions concerned are often proportional to the ionic fractions of these ions. Various definitions of the ionic fraction have been proposed; that used by Herasymenko and Speight<sup>6</sup> has been employed in the present treatment. On this definition, the ionic fraction is the number of gramme-ions of the particular ion in question in unit weight of slag, divided by the total number of gramme-ions of all the assumed species in the same amount of slag, irrespective of the sign of the ions. Clearly, the usefulness of the results obtained from an ionic treatment is dependent upon the particular ionic species assumed to be present, and careful attention must be devoted to this aspect.

### (a) Application to Copper-Oxygen-Phosphorus System

The ionic species present in the slags studied in this work are open to discussion. Those suggested by Chipman and Chang:<sup>7</sup>



are the simplest formulæ and are used in the following interpretation. These formulæ are, however, arbitrary in one respect, for it is recognized that polymerization into chains or ring structures, especially of the metaphosphate ion, may take place in the liquid slag. The consequences of any such polymerization on the treatment given are briefly referred to later. Our reason for preferring the above simple formulæ is the fact that phosphate slags appear to be extremely fluid, which suggests that little polymerization occurs, since the viscosities of slags containing ionic chains, &c., are generally high.

The uncharged ion (molecule)  $P_2O_5$  is likely to be present in appreciable quantity only when the cuprous oxide content of the slag is small, i.e. when the oxygen pressure over the system is very low. No volatilization of  $P_2O_5$  was noted in the present work, so it is unlikely that much free  $P_2O_5$  was present in the slags. As the oxygen pressure increases, it is to be expected that more and more of the phosphorus will be present as  $PO_3^-$  ions, or, at high oxygen pressures, as  $PO_4^{---}$  ions. Since the molecular treatment given above showed that the slags formed in this system are essentially cuprous phosphates, it is reasonable to assume that most of the copper is present as the cuprous ion  $Cu^+$ , although the existence of some cupric ions  $Cu^{++}$  at high oxygen pressures is possible. The only other ionic species likely to be present is the oxygen ion  $O^{--}$ , which, by analogy with current views on silicate slags, exists only in a very small (but not negligible) quantity in the presence of  $PO_3^-$  ions which combine with oxygen ions to form  $PO_4^{---}$  ions.

On the basis of these assumptions, it is possible to write a series of equations between the phosphorus and oxygen contents of the metal and the various ions in the slag. As a convenient starting point, it may be assumed that the phosphorus and oxygen in the metal react to form  $P_2O_5$ , which is present both in the slag and in the atmosphere. In the ensuing treatment it is assumed that the ionic activities are proportional to the corresponding ionic fractions, so that the latter quantities may be inserted in the expressions for the equilibrium constants:



$$K_{10} = \frac{(P_2O_5)}{[P]^2[O]^5}$$

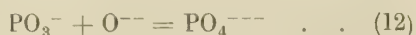
The molecular  $P_2O_5$  thus formed in the slag will be largely converted to  $PO_3^-$  ions, unless the oxygen pressure is very low:



$$K_{11} = \frac{(PO_3^-)^2}{(P_2O_5)(O^{--})}$$

If the cuprous oxide content of the slag is high enough to provide sufficient oxygen ions, a certain amount of

the  $\text{PO}_3^-$  ions thus formed will, in turn, be further oxidized to  $\text{PO}_4^{--}$ :



$$K_{12} = \frac{(\text{PO}_4^{--})}{(\text{PO}_3^-)(\text{O}^{--})}$$

The formation of cuprous ions may be represented by:

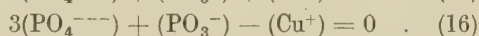


$$K_{13} = \frac{(\text{Cu}^+)^2(\text{O}^{--})}{[\text{Cu}]^2[\text{O}]}$$

Since the activity of copper in the system is essentially unity,

$$[\text{Cu}] = 1 \quad (14)$$

Two other relations follow from the stoichiometry and electroneutrality of the slags. Neglecting  $(\text{O}^{--})$  and  $(\text{P}_2\text{O}_5)$ , which are small, there are obtained:



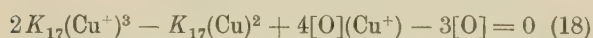
These seven equations completely describe the system, and it may be noted that, in accordance with the Phase Rule, they involve eight unknown concentrations, i.e. there is one compositional degree of freedom.\*

Some useful relations may be derived from the above equations. In particular, from equations (12), (13), and (14), there is obtained:

$$[\text{O}] = \frac{1}{K_{12}K_{13}} \cdot \frac{(\text{Cu}^+)^2(\text{PO}_4^{--})}{(\text{PO}_3^-)} \quad (17)$$

$$= K_{17} \cdot \frac{(\text{Cu}^+)^2(\text{PO}_4^{--})}{(\text{PO}_3^-)}, \text{ where } K_{17} = \frac{1}{K_{12}K_{13}}$$

and from elimination of  $(\text{PO}_3^-)$  and  $(\text{PO}_4^{--})$  between equations (15), (16), and (17) there is derived:



Provided that  $[\text{O}]$  is not too large,  $(\text{Cu}^+)$  may be found from (18) with the aid of Newton's rule:

$$(\text{Cu}^+) = \frac{0.5 + [\text{O}]\{6 - 8(\text{Cu}^+)\}}{K_{17}} \quad (19)$$

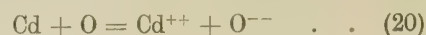
Many other relations can, of course, be derived from equations (10)–(16), but the above appear to be the only useful ones in the present instance.

#### (b) Application to Copper-Oxygen-Cadmium-Phosphorus System

Since cadmium has only one valency state, it seems reasonable to suppose that it is present in copper-oxygen-cadmium-phosphorus slags as  $\text{Cd}^{++}$ . On this assumption a number of equations may be derived for the equilibrium relations in this system in a manner analogous to that used above for the copper-oxygen-phosphorus system.

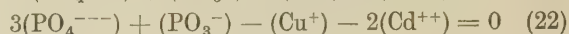
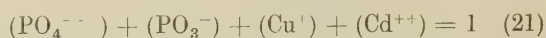
In the first place, equations (10)–(14) apply without change to the cadmium-containing system. An addi-

tional equation results from the oxidation of cadmium in the metal to form  $\text{Cd}^{++}$  ions in the slag:



$$K_{20} = \frac{(\text{Cd}^{++})(\text{O}^{--})}{[\text{Cd}][\text{O}]}$$

The stoichiometry and electroneutrality relations are:



again neglecting  $(\text{O}^{--})$  and  $(\text{P}_2\text{O}_5)$ .

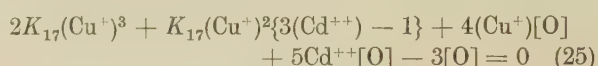
The following equations may be derived from those cited above. From equations (12) and (20) there is obtained:

$$[\text{Cd}][\text{O}] = \frac{(\text{Cd}^{++})(\text{PO}_4^{--})}{K_{12}K_{20}(\text{PO}_3^-)} \quad (23)$$

and by eliminating  $[\text{O}]$  and  $[\text{O}^{--}]$  from (20) by means of equation (13):

$$[\text{Cd}] = \frac{K_{13}}{K_{20}} \cdot \frac{(\text{Cd}^{++})}{(\text{Cu}^+)^2} \quad (24)$$

Also from (13), (21), and (22):



Unfortunately, this last equation cannot readily be solved by Newton's rule or otherwise.

#### (c) Calculation of Ionic Fractions

The ionic fractions of the various ions were calculated by a method similar to that described by Herasymenko

TABLE IV.—Examples of Ionic Fraction Calculations

Melt No.	Slag Analysis, %	Gramme-Ions of Oxygen Available from Metal Oxides	Gramme-Ions of Oxygen Consumed by Anions	Total Number of Gramme-Ions	Ionic Fraction
(i) Copper-Oxygen-Phosphorus System					
17	$\text{P}_2\text{O}_5$ 41.8	...	$\frac{41.8}{142} = 0.294$	$\text{PO}_3^- + \text{PO}_4^{--} = 0.589$	
	$\text{Cu}_2\text{O}$ 53.5	$\frac{53.5}{143} = 0.374$	...	$\text{Cu}^+ \quad 0.748$ $\text{PO}_4^{--} \quad 0.080$ $\text{PO}_3^- \quad 0.609$	$\text{Cu}^+ \quad 0.559$ $\text{PO}_4^{--} \quad 0.060$ $\text{PO}_3^- \quad 0.381$
				Total 1.337	
(ii) Copper-Oxygen-Cadmium-Phosphorus System					
22	$\text{P}_2\text{O}_5$ 44.9	...	$\frac{44.9}{142} = 0.316$	$\text{PO}_3^- + \text{PO}_4^{--} = 0.632$	
	$\text{Cu}_2\text{O}$ 20.9	$\frac{20.9}{143} = 0.146$	...	$\text{Cu}^+ \quad 0.292$ $\text{PO}_4^{--} \quad 0.093$ $\text{PO}_3^- \quad 0.539$	$\text{Cu}^+ \quad 0.246$ $\text{PO}_4^{--} \quad 0.078$ $\text{PO}_3^- \quad 0.454$
	$\text{CdO}$ 33.6	$\frac{33.6}{128} = 0.263$		$\text{Cd}^{++} \quad 0.262$	$\text{Cd}^{++} \quad 0.222$
				Total 1.186	

N.B.—Oxidation of  $\text{P}_2\text{O}_5$  is considered to be  $\text{P}_2\text{O}_5 \rightarrow \text{PO}_3^- \rightarrow \text{PO}_4^{--}$ , i.e. the oxygen necessary to satisfy the  $\text{PO}_3^-$  ion is taken before the  $\text{PO}_4^{--}$  ion can form.

and Speight;<sup>6</sup> the method of calculation is illustrated by two examples in Table IV. The treatment of the small amount of alumina present in the slags posed some difficulty, but after trials of various methods it was

components. Hence, after fixing the temperature, one degree of compositional freedom remains.

\* Application of the condensed Phase Rule:

$$P + F = C + 1$$

yields  $F = 2$ , since the system consists of 2 phases and contains 3



decided to assume that all the alumina was present as alumina molecules rather than as  $\text{AlO}_3^{---}$  or  $2\text{Al}_3^+ + 3\text{O}^{--}$ . The alumina was therefore ignored in subsequent calculations. Poor plots were obtained from the initial calculations, which were traced to marked scatter in the analyses of the oxygen contents of the metal samples.

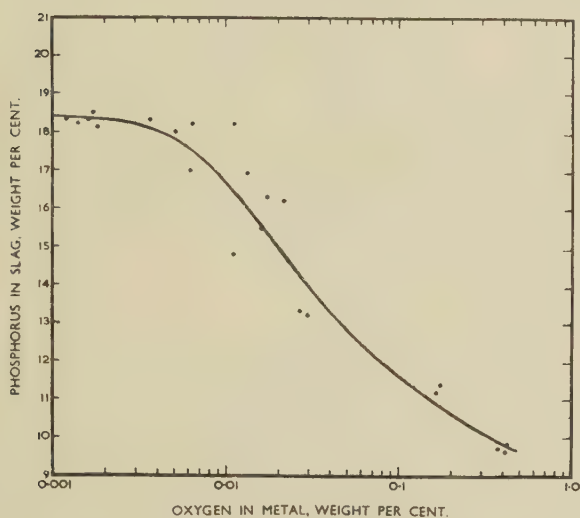


FIG. 8.—Copper-Oxygen-Phosphorus System: Relationship Between the Oxygen Content of the Metal and the Phosphorus Content of the Slag.

To reduce this source of scatter, these oxygen contents were plotted against the phosphorus contents of the relevant slags and a smooth curve drawn between the points (Figs. 8 and 9). Values for the oxygen contents

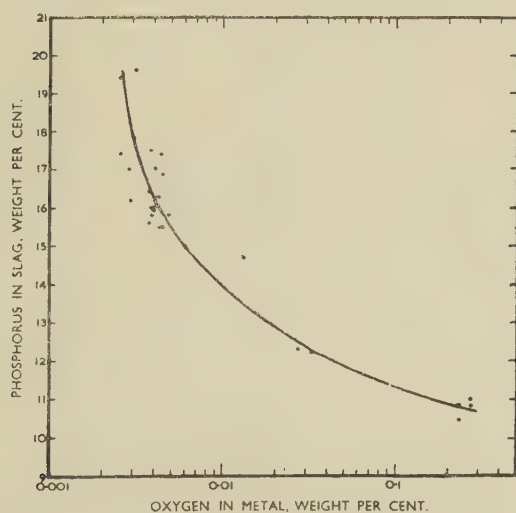


FIG. 9.—Copper-Oxygen-Cadmium-Phosphorus System: Relationship Between the Oxygen Content of the Metal and the Phosphorus Content of the Slag.

of the metal samples were taken from these smoothed curves and used in preference to the analytical results in subsequent calculations.

#### (d) Discussion of Results

##### (i) Copper-Oxygen-Phosphorus System

According to equation (17), a straight line should be obtained on plotting the oxygen content of the metal phase against the quantity:

$$\frac{(\text{PO}_4^{---})(\text{Cu}^+)^2}{(\text{PO}_3^-)},$$

and Fig. 10 shows that the expected straight line passing through the origin was, in fact, obtained from the present results.

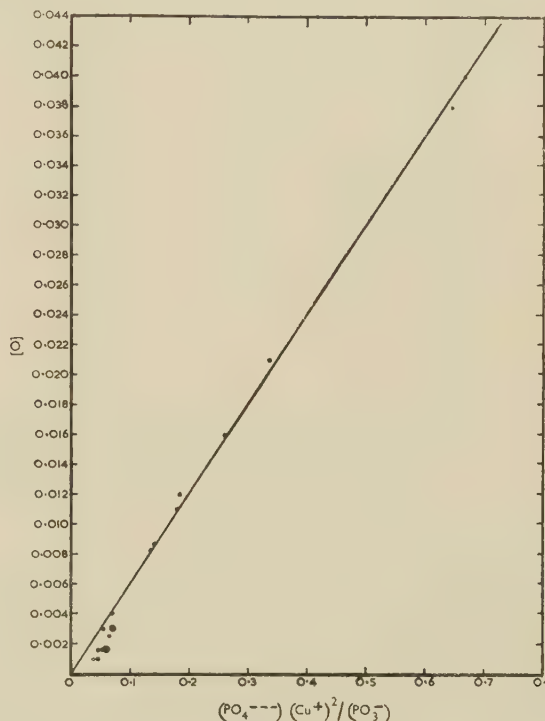


FIG. 10.—Copper-Oxygen-Phosphorus System: Plot of [O] Against  $\frac{(\text{PO}_4^{---})(\text{Cu}^+)^2}{(\text{PO}_3^-)}$ .

Equations (18) and (19) predict that a straight line should also result from plotting the ionic fraction of copper in the slag ( $\text{Cu}^+$ ) against the product:

$$[\text{O}]\{6 - 8(\text{Cu}^+)\}.$$

A reasonably good line was obtained from the present results, although there were two "wild" points (Fig. 11), but this line did not pass through the point  $(\text{Cu}^+) = 0.5$ ,  $[\text{O}]\{8 - 6(\text{Cu}^+)\} = 0$ , as required by equations (18) and (19). The reason for this is obscure.

##### (ii) Copper-Oxygen-Cadmium-Phosphorus System

Less satisfactory plots were obtained from the ionic fractions of the slag constituents in this system, partly because of a wide gap in the slag composition studied experimentally. For example, in a plot of the oxygen content of the metal against:

$$\frac{(\text{PO}_4^{---})(\text{Cu}^+)^2}{(\text{PO}_3^-)}$$

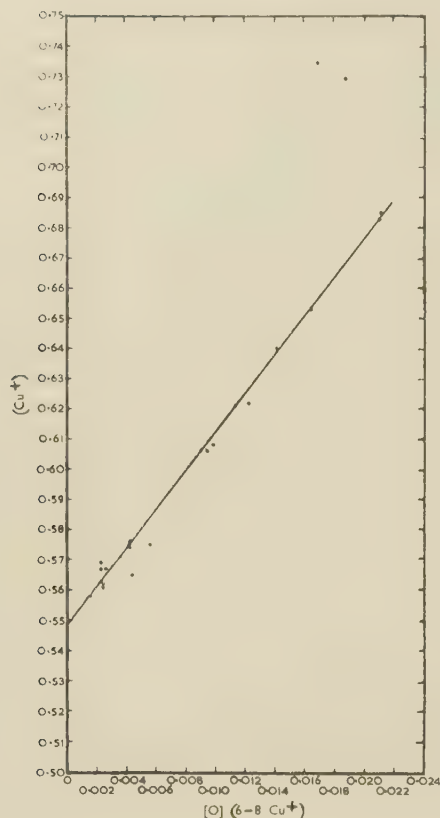


FIG. 11.—Copper-Oxygen-Phosphorus System: Plot of  $(\text{Cu}^+)$  Against  $[\text{O}] \{6-8(\text{Cu}^+)\}$ .

nearly all the points fell in a rather scattered group near the origin (Fig. 12), the remaining two points being located some distance away. It is true that a straight line can be drawn through the origin which passes close

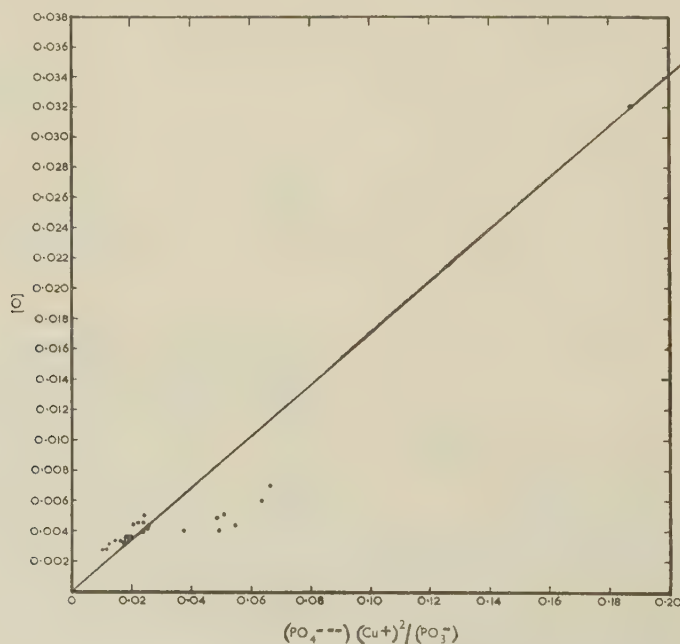


FIG. 12.—Copper-Oxygen-Cadmium-Phosphorus System: Plot of  $[\text{O}]$  Against  $\frac{(\text{PO}_4^{---})(\text{Cu}^+)^2}{\text{PO}_3^-}$ .

to these two points and through the scatter group near the origin, but clearly a linear relationship between the above two quantities cannot be firmly established without further work that would enable more points to be located in the middle of the composition range.

These remarks are also true of the plot in Fig. 13 of the product of the cadmium and oxygen contents of the metal,  $[\text{Cd}][\text{O}]$ , against the quantity:

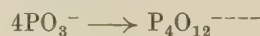
$$\frac{(\text{PO}_4^{---})(\text{Cd}^{++})}{(\text{PO}_3^-)}$$

linear relationship between which is predicted by equation (23).

The only other relationship plotted was that between the cadmium content of the metal  $[\text{Cd}]$  and the quotient  $(\text{Cd}^{++})/(\text{Cu}^+)^2$ . As Fig. 14 shows, the points are very scattered, but show a linear trend.

### (iii) The Effects of Polymerization

As mentioned earlier, it is possible that in these slags certain of the ions, in particular the metaphosphate ion  $\text{PO}_3^-$ , polymerize to form chains or ring structures. This would not only affect the calculation of the ionic fractions, but would also change the equations for the equilibrium constants. Study of the crystal chemistry of metaphosphates indicates that the most likely polymerization is:



The ion  $\text{P}_4\text{O}_{12}^{---}$  is an eight-membered ring. Altering the above calculations to take account of this polymerization did not give helpful results, however, as it was found to convert the plots in Figs. 10-14 from straight lines into curves. Smooth curves might be expected if the polymer  $\text{P}_4\text{O}_{12}^{---}$  broke down in several overlapping stages to  $\text{PO}_4^{---}$ , but if this model were



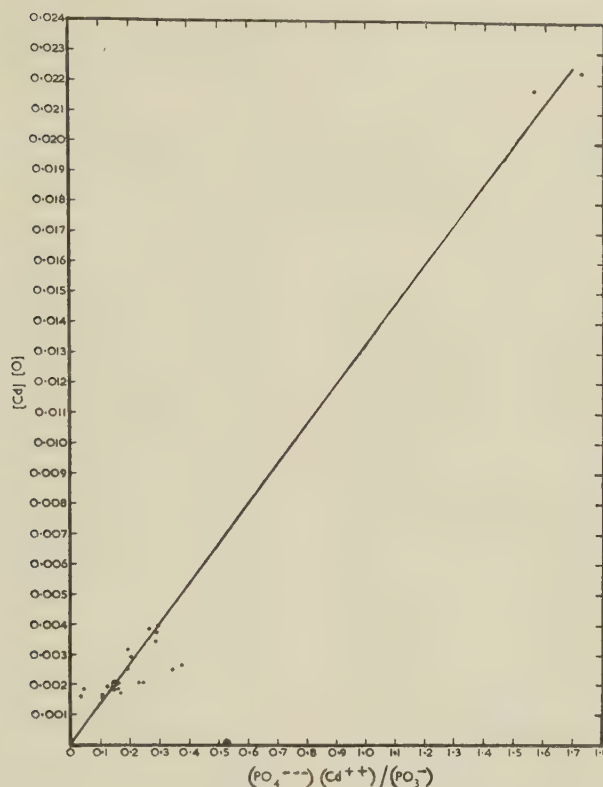


FIG. 13.—Cadmium-Oxygen-Copper-Phosphorus System : Plot of  $[Cd][O]$  Against  $\frac{(PO_4^{---})(Cd^{++})}{(PO_3^-)}$ .

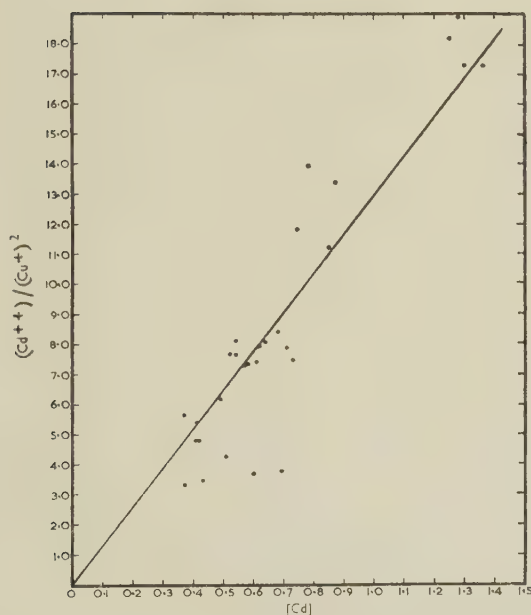


FIG. 14.—Copper-Oxygen-Cadmium-Phosphorus System : Plot of  $[Cd]$  Against  $\frac{(Cd^{++})}{(Cu^+)^2}$ .

correct, the linear relationships deduced from equations (10)–(25) would not be obeyed.

#### (e) Conclusions

Although this attempt at an ionic interpretation of the present results has not established with any certainty simple relationships between the compositions of the metal and slag phases in either of the systems considered (the relation given by equation (12) and plotted in Fig. 10 is possibly an exception), the plots in Figs. 10–14 are on the whole quite encouraging. However, more information will be necessary, particularly about the behaviour of the copper-oxygen-cadmium-phosphorus system in the middle of the composition range, before the theory can be accepted.

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## Metallurgical Aspects of the Control of Quality in Non-Ferrous Castings\*

Dr. W. A. BAKER,† F.I.M. (Member), who acted as Rapporteur, in introducing the papers said that in the casting industry, as in others in the metallurgical field, it was rarely possible today to measure the metallurgical variables influencing quality with the precision and speed necessary for anything approaching closed-loop control. In these circumstances the authors, in common with the authors of papers presented to earlier symposia on control of quality, had been obliged to describe the metallurgical aspects of non-ferrous casting practice in considerable detail, calling attention to the effects of the many variables involved and describing procedures adopted to keep them as constant as possible, while for the most part tacitly admitting that immediate and individual control of each variable was not attainable. One of the most fruitful topics for discussion would be the consideration of rapid techniques capable of measuring some aspect of metallurgical quality in time to permit adjustments to be made to the relevant variables affecting that quality.

He discussed the more important metallurgical variables brought out in the Symposium, with appropriate references to each paper, and invited members to make contributions to the discussion based on their practical experience.

Dr. Baker referred to the effects of composition on the end-use properties of the finished casting and on other—notably casting—characteristics, affecting the ease with which good-quality castings could be made consistently, and commented that techniques capable of detecting departures in composition from the desired norm, or of effects attributable to that variable, in time to rectify matters before the metal was poured would be an invaluable aid. In this connection much still remained to be learned about the effects of impurities; for example manufacturers still tended to make certain alloys from virgin metals to be on the safe side.

One of the most important aspects of composition was the gas content of the metal, and it would be useful to discuss techniques available for controlling the gas content of non-ferrous melts and particularly techniques available for the measurement and correction of this variable before the metal was cast. In most cases the authors had described techniques adopted to ensure that the gas content of the melt was reduced to a minimum, but at one or two points in several of the papers it was shown that gas dissolved in the melt before casting, or absorbed by the metal during solidification in the mould, could aid rather than hinder the production of high-quality castings.

One of the few variables for which accurate and rapid methods of measurement were in most cases available was temperature, the exception being for copper alloys for which no completely satisfactory technique had been developed. He invited members to exchange experiences on this topic and particularly to discuss the potential value of recording pyrometers as a means of obtaining registers of the time factors which frequently are vitally important variables affecting the quality of the product. For example, the time lapse between completion of some melt treatment and the transfer of the metal to the mould was frequently all-important, and sometimes also the lapse of time between preparing a mould and

filling it. For example, it was not uncommon to use torches to skin-dry moulds, and these might set up favourable or unfavourable gradients in the mould cavity, so that the period of time between this operation and pouring the casting might be highly significant.

He referred to the functions of test-bars and to the suggestion in some of the papers that test-bars designed to provide information for an acceptance inspection procedure would not necessarily give the founder all the information he would like to have in aiding him to control quality. One of the papers contained interesting examples of the application of statistical treatment of test-bar and other test results as a means of detecting inadvertent changes in practice or of pointing to the existence of some hitherto unsuspected factor affecting quality.

Another vitally important variable was the transfer of the metal to the mould and, bearing in mind the human element involved, he invited the members to consider the extent to which this was under adequate control in normal practice, referring by way of example to the very large effects which chance draughts might have on the rate of cooling of open-top feeders. Discussion of the steps taken to ensure that a chosen and proven gating and feeding technique was in fact rigidly followed for every casting might be well worth while.

There was obviously ample ground for discussion on methods of inspection of the finished casting, of the interpretation of the results, and of the methods adopted for recording these and using them to make appropriate changes in the numerous variables involved in the casting process.

Several of the authors stressed the importance of close co-operation between the user and the founder at the earliest possible stage of casting design, and he hoped that the contributors to the discussion would reinforce this point, because it was undoubtedly one of the major factors affecting both the level of quality attainable in the finished product and the consistency which might be expected under given conditions of melting and casting.

Mr. F. HUDSON,‡ F.I.M. (Member): Any criticism which I have to make of the papers is related not to the information which they contain, but to that which has been omitted. Two factors come prominently to mind which have a fundamental bearing on the control of quality in non-ferrous castings, namely, the design and the properties of the casting.

A casting is born on the drawing-board, and of the many variables with which the foundryman has to contend design is undoubtedly the most important. Far too many castings are badly designed, not because of the engineers who conceived them but because of the founders who persist in trying to make them on the basis of "Let's have a go and hope for the best."

The remedy is obvious. Everyone concerned must take a greater interest in the design of castings, make a point of learning as much as possible about the subject, and then see that the knowledge gained is applied in actual practice. This will demand more intimate co-operation between founder and engineer than exists today. The British Steel Founders'

\* Joint discussion on papers Nos. 1744-1746, 1749-1752, and 1754 (*Journal*, this vol., pp. 209-254, 265-338, 361-366) held in London on 1 May 1957.

† Research Manager, British Non-Ferrous Metals Research Association, London.

‡ The Mond Nickel Co., Ltd., London.



Association and the Centre Technique des Industries de la Fonderie have made a useful start in this direction, and it is hoped that this may be carried still further by the work now being done by Sub-Committee T.S.50 of the Technical Council of the Institute of British Foundrymen.

The subject of casting design has not been given the emphasis it deserves in the majority of the papers, and I would like strongly to support Mr. Sharp in the statement on p. 333, when he says:

"Much can be done at the early stages of designing a casting and die to ensure that a high standard of quality is subsequently maintained. It cannot be too strongly emphasized that such design considerations are essential features of positive quality control. If they are not taken into account, quality control becomes no more than an inquest after the event, to sort out the good from the bad, instead of serving its real purpose of ensuring that only good castings are produced."

In designing a casting the engineer in addition to meeting the needs of the foundryman, must take into account the stresses that will ultimately be imposed in service. To do this satisfactorily requires information on the properties of castings, of which very little is available. For the majority of engineering requirements the stresses involved are low and the factor of safety high, so that reliable information on properties may not be essential. In such cases the designer obtains the guidance he needs from past experience and from such data as may be forthcoming on the mechanical properties of separately cast test-bars—which may, or may not, be representative of the casting.

It is quite another story in designing castings which must operate under specialized service conditions at high stresses with a low factor of safety, and where past experience is limited or does not exist. The engineer cannot afford to take chances, and reliable data must be made available on the properties of the actual castings themselves. A certain amount has been done in this direction by some of the more progressive foundries producing alloy steel and light alloy castings for aircraft, and the results have proved extremely valuable, not only in promoting new developments but also in providing greater confidence in the quality of the castings, which, unfortunately, the engineer does not always possess.

As the years go by there will be an increasing need for more data on the properties of castings, and foundries will have to devote much greater attention to this subject. In other words, foundries will have to sell castings and not test-bars. Without such information it is difficult to see how casting quality can be fully assessed. I had hoped that this matter might receive some consideration, but most of the authors have avoided any reference to the properties of the castings themselves.

One of the important factors which affect the mechanical properties is the influence of section thickness upon strength and ductility. From what little information is at present available, it is believed that castings in alloys with a short freezing range, such as steel, aluminium bronze, high-tensile brass, certain light alloys, &c., can be produced with properties approaching those obtainable from separately cast test-bars. With alloys having a long freezing range, such as cast iron, tin-bronze, gun-metal, &c., the properties of castings may be very much less than those obtainable from separately cast test-bars, if the thickness of the casting is greater than the test-bar. In the latter case particularly, further information is badly needed about the effect of section on properties. Knowledge of this kind is essential for the ultimate realization of a properly designed casting. It can be obtained by cutting test-bars from production castings, by the use of experimental step-bar castings, or by testing castings to destruction. To obtain further information, investigations have been under

way in our laboratory for some time with a step-bar casting having sections varying from  $\frac{1}{2}$  to 4 in. in thickness. Great care is taken to ensure that the casting is fully fed and as sound as possible.

I should like to quote some results obtained from test-pieces cut from these step-bar castings for two old-established copper-base alloys which have been used in this country for many years, namely, Admiralty gun-metal containing copper 88, tin 10, and zinc 2%, and 85 : 5 : 5 : 5 gun-metal.

In the case of Admiralty gun-metal, the tensile strength in the 1-in.-thick section was 20.3 tons/in.<sup>2</sup>; this fell to 14.9 tons/in.<sup>2</sup> in a 4-in.-thick section, a decrease of about 26%. With 85 : 5 : 5 : 5 gun-metal, the tensile strength in similar sections fell from 16 to 7.8 tons/in.<sup>2</sup>, a decrease of about 50%. The fall in tensile strength as casting section increases is due mainly to the incidence of shrinkage porosity, and it is evident that Admiralty gun-metal is a better alloy than 85 : 5 : 5 : 5 gun-metal when maximum strength in heavy sections is desired. I wonder how many foundries and metallurgists are aware of this difference in behaviour between two of the most common and widely used copper-base foundry alloys. Yet how is it possible, without such information, fully to assess what might constitute quality in a casting?

It must never be forgotten that the control of quality in non-ferrous castings begins on the designer's drawing-board and ends with the ability of the founder to produce a casting with known properties to meet the needs of the user.

Mr. R. J. M. PAYNE,\* B.Sc., F.I.M. (Member): Mr. Hudson has remarked on the absence of information in these papers on the castings themselves and on the standard of quality actually attained. Further information of this kind is obviously essential if we are to appreciate the extent to which the methods of control applied are useful. It is, moreover, in my opinion, inevitable that there will be an increasing pressure on foundrymen to prove that the quality of their castings is good. I believe that in some American materials specifications foundries are called upon to show that stated mechanical properties are, in fact, achieved.

I do not know why there has been this reluctance on the part of the authors dealing with specific metals to give information on the properties of the actual castings. Perhaps it was felt that this aspect lay outside the scope of the Symposium. Dr. Emley and Mr. Fisher have, however, given some results on cut-up tests on magnesium castings, and if those do nothing more, they may at least dispose of the suspicion of some users that, where there is any difference between the properties of the separately cast test-bars and castings, that difference is always in the downward direction. This is a viewpoint encouraged by the wording of the cautionary phrase with regard to the properties of castings which appears in the materials specifications.

I also examined the papers to find some indication of the degree to which mechanical properties are affected by the section factor, as this differs greatly with different alloys. For example, a 4-in. section, which seriously affects the properties of some aluminium-base and magnesium-base alloys, has scarcely any influence on the properties of manganese bronzes and aluminium bronzes. Not only are there differences in the effect of section as between alloys of different types, but also between alloys having the same basis metal. This is particularly marked where one alloy contains brittle intermetallic compounds and the other does not, e.g. RZ5 and Z5Z magnesium alloys.

With regard to the paper by Dr. Emley and Mr. Fisher, it should be emphasized that the conclusion reached by Skelly and Sunnucks, to which they refer on p. 251, that healed hot tears are without effect on the tensile and creep properties, relates only to the particular alloy mentioned, ZRE1. The effect of healed hot tears on other alloys may be quite con-

\* Chief Research Metallurgist, J. Stone and Co. (Charlton), Ltd., London.



siderable, TZ6 and RZ5 being examples. Secondly, a blue colour on magnesium-aluminium alloy castings should not be taken too lightly. It indicates a segregation not only of magnesium silicide, which is probably quite unimportant, but also of magnesium-aluminium compound in much greater amounts. As the authors note, it also marks the presence of a coarse grain, and the effect of coarse grain on strength may be very considerable.

Dr. V. KONDIC,\* B.Sc.: The control of castings involves three factors: the metal, the mould, and the human element. Whilst I can appreciate the exclusion of the last of these, I am surprised that the plan of the Symposium excluded the mould, especially as so much has happened in the last fifteen years or so in this field.

A second criticism concerns the avoidance by the authors, or by most of them, of the thermodynamic approach. I cannot think of any more pertinent way of summarizing what is happening in the melting and casting of metals than by employing the science of thermodynamics.

I wish to make some specific points, and propose to take the paper by Mr. Ruddle and Mr. Cibula as the most comprehensive, and refer to other papers as the different questions arise. I feel that a student reading about the subject for the first time would get the impression from this paper that everything in the field of melting and casting is well under control, that all the principles are known, and that all the foundryman has to do is simply to apply them. I submit that, in fact, the position is not as good as that; there are a number of questions to which we have no satisfactory answers.

First, there is the question of flow. Reading the paper by Mr. Ruddle and Mr. Cibula, one would come to the conclusion that if it was desired to calculate how long it would take to fill the mould for a given casting, or—what to my mind is even more important—to know the condition of the metal in the gating system, plenty of information is available; in fact, not one of the subsequent papers makes use of such data. I suggest that knowledge about the time of flow and the condition of flow is very scarce and only touches the fringe of the subject, and that it is not possible to make much use of it as yet.

The second subject which these authors mention is fluidity. I am very surprised that they identify the spiral fluidity with the casting fluidity. I have, on the contrary, come to the conclusion that the spiral fluidity test is one of the most manifestly misleading tests used by foundrymen, and that in fact it is of little practical use, if any at all, though it has certain metallurgical applications. Mr. Wood and Mr. Gregg have shown that this is the case for nickel-base alloys, and other experience points in the same direction.

In this connection I should like to ask Mr. French exactly what he means when he says that aluminium promotes the fluidity of certain copper-base alloys. Does he mean the spiral or the casting fluidity? I should also be glad to know whether Mr. Carless in his experience of aluminium alloy founding can recall cases of alloys possessing different casting fluidity, though of the same composition and cast at the same temperature. Does it ever arise in aluminium founding that a given alloy may exhibit inferior fluidity, assuming that the temperature and composition are satisfactory?

The data available on heat flow in sand moulds are so inadequate that we have no chance whatever, until further work is forthcoming, of calculating heat transfer in the case of shaped castings. As yet, we cannot even, with much degree of accuracy, estimate how long a casting of the size and shape of a glass tumbler would take to solidify, and castings made in foundries are of much more complicated shape than that. Probably there is some hope of calculating heat flow in risers, but even there, as anyone who has studied the subject must realize, the position is far from satisfactory.

The aspect of the feeding of castings, treated at length by Ruddle and Cibula, is essentially that of heat transfer. Hardly any data are available on the volume changes which take place in an alloy as a function of composition and temperature. This again is a field in which much more work is required. Heat transfer is only one aspect of the subject, and the volume data are badly needed.

The question of gases in metal founding has been treated by several authors. What is important so far as the foundry is concerned is the problem of measuring the gas content while the metal is still in the pot. It has been suggested that Ransley's test will probably provide the answer eventually. Certainly for aluminium alloys this test at the moment looks most promising, but for copper-base and nickel alloys, the value of this test has yet to be proved, and alternative solutions of the problem of measuring the gas content of an alloy in the foundry are badly required. One or two authors refer to the use of the Pfeiffer test. This test is so simple that everyone is tempted to make use of it, but it is one of the most "touchy" tests which can be used in the foundry, because it is so sensitive to the variables inherent in the apparatus. I have found this test extremely unreliable.

The view is now generally accepted that the grain-size of a casting is controlled by a phenomenon termed heterogeneous nucleation. Mr. Cibula is one of the main exponents of that view in this country, and this theory is widely accepted abroad. In other words, the grain-size of a casting is determined by nuclei added to the melt intentionally, or by those that happen to be already there. From some researches which we have carried out, and from reading the more recent literature, I have come to doubt very much this simple explanation of the origin of grain-size in castings. Heterogeneous nucleation no doubt plays a part, but in my view it is not the main factor responsible. What we normally call grain-refinement effect is not attributable to the nucleation factor alone, and in fact, I would accord it only a second place.

I should also like to have the authors' views on why they carry out grain refinement, and, when they do so, which phase are they trying to refine? Most foundry alloys are complex alloys, and there is the question of whether it is the primary or the secondary phase.

It is also high time that we had an accepted standard of grain-size for purposes of reference. Most papers on the subject are difficult to interpret, because the units of grain-size are not given.

Finally, there is the question of test-bars. Here we have a control test which requires a good deal of control, and we can hardly interpret the results without statistical aids. A comprehensive study of test-bars is a sadly neglected field of research.

Mr. CARLESS (*in reply*): Dr. Kondic has raised the question of comparative fluidity in various aluminium alloys and asked whether any significant difference due to chemical additions is known. In general, the answer, so far as our own practice is concerned, is "No", but there may possibly be differences in one or two cases. The first of these is the L33 silicon alloy, in which the degree of fluidity is greatly dependent on the amount of modification; I suppose this does constitute a change in chemical composition, although a very slight one, in sodium content. With over-modified material, however, we do not obtain the same fluidity.

The other case is more subtle. It concerns two alloys not in general use, but which we employ a great deal. These are aluminium-base alloys containing 5% copper, 1-1.6% nickel, and additions of manganese and other elements, including a rather unusual one, antimony, and, in the second case, zirconium. These alloys exhibit all the characteristics of an aluminium-copper alloy of this type and are not what we term very fluid alloys. They are difficult foundry alloys, and

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one of the major problems in making sand castings of any complexity consists in their indifferent feeding characteristics. We have experienced a great deal of trouble with castings of this composition, and the answer was found to lie in the addition of proprietary grain-refiners in quite large amounts. These did not refine the grain-size a great deal—this was normally satisfactory in any case—but they did have the effect of altering the fluidity and also the feeding characteristics. I do not know why, and I do not think that anyone who has had experience of these alloys does know the reason. The most careful inverse-rate cooling curves have been plotted, and no perceptible difference can be detected in interval of freezing or in other features.

We find grain refining advantageous largely for the control of heavier-section castings, and it is, of course, normally a great help in castings which have to be pressure-tested.

On the question of whether test-bars are representative or otherwise, as Dr. Baker says, as a general rule they are considered to be a symbol of the quality of the metal being used. Despite Dr. Kondic's remarks, I do not see how it would be possible to link them more specifically with the various designs of castings.

As regards the comments on the Pfeiffer apparatus, we should use a better method if one were available. We employ the B.N.F. reduced-pressure modification of this test. It can be misleading; for instance, if too low a pressure, below the order of 20 mm., is used, it is possible to get fictitious results with LM 10,\* owing to a slight volatilization of magnesium, but in the 40–20-mm. range I think that it is a very good test. The Ransley apparatus is now being put on the market commercially and one is available to us. At the moment we feel we need further experience in its use before we can consider it as a really dependable foundry tool. At present we are getting variable results.

Mr. CIBULA (*in reply*): Although, as Dr. Kondic remarks, quantitative data on heat flow and metal flow in sand moulds are lacking, with the consequence that an accurate estimation of pouring and solidification times can seldom be made, sufficient information is available to indicate how running and feeding methods may be improved. The value even of qualitative information for this purpose should not be underestimated, and we have tried to indicate in our paper what conclusions may be drawn about the design of the feeders and of various features of the running and gating system.

The term "casting fluidity" is often applied to two properties—the ability of the metal to flow *through* narrow sections, and the ability of the metal to penetrate *into* sharp corners. These properties are controlled by quite different factors, as a recent paper by Wood and Gregg † made clear. The fluidity spiral, as normally used, measures the first of these properties, and clearly the results are relevant only to certain types of defects in castings; fluidity in this sense is largely controlled by the heat content of the metal when cast, and probably, though to a lesser extent, by the mode of solidification of the alloy. The penetration into sharp corners is much more affected by the surface properties of the alloy, particularly the presence of tenacious films of oxide, and these properties are not assessed at all sensitively by the length of the fluidity spiral; a different type of test is needed, such as that described by Wood and Gregg, or another at present in use in the laboratories of the British Non-Ferrous Metals Research Association.

It is difficult to reply to Dr. Kondic's remarks on grain refinement without a knowledge of the experimental results to which he refers. In the absence of this information, it must suffice to say that the grain-size of a casting may be controlled quite adequately for industrial purposes by making a grain-refining addition which can be shown to precipitate fine particles of a specific compound in the liquid metal.

Dr. E. SCHEUER ‡ (Member): I wish to support very strongly what has been said about the necessity for studying the mechanical properties of castings in detail. I think that an important approach has been neglected, and I do not know of any way of replacing it by theoretical studies. The engineers need actual data, and the only convincing method is to study the distribution of strength at various locations in the casting.

I should also like to draw attention to the case of a deliberately maintained gas content in castings. Ruddle and Cibula (pp. 284–285) discuss this aspect, but do not mention methods of control.

It is known that in a number of instances a certain gas content is not only tolerable, but indeed necessary in order to obtain usable castings under practical production conditions. This applies to sand castings of many copper alloys § and to gravity die-castings in certain aluminium alloys.¶ In the case of copper alloys, a suitable gas content is introduced by metal/mould reaction; in the case of aluminium alloys the gas is introduced mostly by plunging into the melt compounds which liberate hydrogen on contact with liquid aluminium. The disadvantages of this latter method are well known. They are connected with the uncertainty of reproducing consistently a gas content other than saturation by the plunging method, and with the rapid loss of hydrogen from the melt after the end of the reaction at the comparatively high concentration required.

The workers at the B.N.F.M.R.A. have suggested a method of maintaining a desired hydrogen concentration in an aluminium melt by bubbling through it a mixture of hydrogen and nitrogen of suitable composition, keeping at least a part of the surface of the bath covered by a hood.¶ We have proposed a simplification of this method, based on bubbling undiluted hydrogen through the melt and establishing a stationary hydrogen concentration in the bath which is regulated (other conditions being constant) by the rate of bubbling, the rate of intake of hydrogen from the bubbles being balanced by the rate of loss from the unprotected top surface of the melt).\*\*

Fig. D3 (Plate LXXVIII) shows the apparatus, consisting of the hydrogen cylinder with the reducing valve, flowmeter, and distributor. In this arrangement, working with a 250-lb. bale-out pot, a bubbling rate of the order of 1–2 l./min. (2.1–4.2 ft.<sup>3</sup>/hr.) is sufficient to compensate for shrinkage losses as against a rate of 3–5 l./min. (6–10 ft.<sup>3</sup>/hr.) producing saturation. Fig. D1 shows the stabilization of the gas content obtained in a normal bale-out furnace. The gas content is expressed in an arbitrary scale based on visually estimated percentage voids in the sectioned vacuum solidification sample.

We find that for given dimensions of the bath this method gives a sufficient consistency and reproducibility for practical purposes, and allows the gas content to be kept at the lowest level required for compensation of shrinkage defects.

Fig. D2 is a graph showing the relation between the percentage of castings with shrinkage defects plotted against bubbling rate, as an arbitrary measure of gas content. The

\* The LM alloys referred to in the discussion are covered by B.S. 1490.

† D. R. Wood and J. F. Gregg, *Brit. Foundryman*, 1957, 1, 2.

‡ Chief Metallurgist and Head of Laboratories, International Alloys, Ltd., Aylesbury, Bucks.

§ W. A. Baker, F. C. Child, and W. H. Glaisher, *J. Inst. Metals*,

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1944, 70, 373.

¶ "The Secondary Aluminium Industry in the U.S.A." (Report of O.E.E.C. Technical Assistance Mission No. 19), para. 124, p. 41. 1952: London (H.M. Stationery Office).

¶ Brit. Patent No. 544,560.

\*\* Brit. Patent No. 685,075.

experimental points have been determined by raising and lowering the bubbling rate several times.\*

In the examination of the effect of gas content on shrinkage defects, we have found a hot-spot die,† shown in Fig. D4 (Plate LXXVIII), very useful. It reproduces faithfully the shrinkage defects found in actual castings (Figs. D5 and D6, (Plate LXXVIII)) and can be operated conveniently on a laboratory scale.

small proportion of the surface area. The turbulence is confined to this region, and there is very little loss of gas from the surrounding quiescent surface, even when, as in the gravity die-casting process, the operator periodically skims the surface and bales out a quantity of metal for casting. In these conditions, if we pass a suitable nitrogen/hydrogen mixture and plot gas content against time, we obtain a stable gas content in about 20 min., the same result being attained

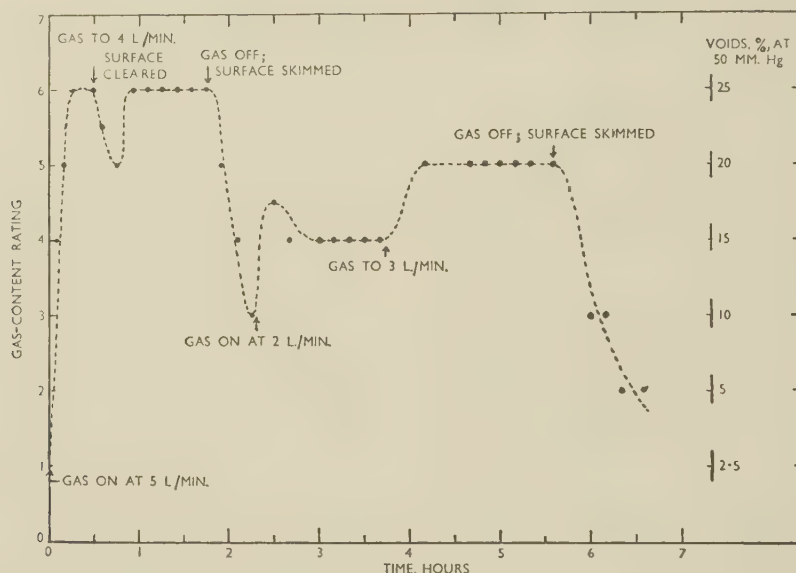


FIG. D1.—Gas-Content Levels Obtained by Varying the Hydrogen Flow Through a 250-lb. Bale-Out Melt of LM4 Alloy<sub>2</sub> at 750° C.

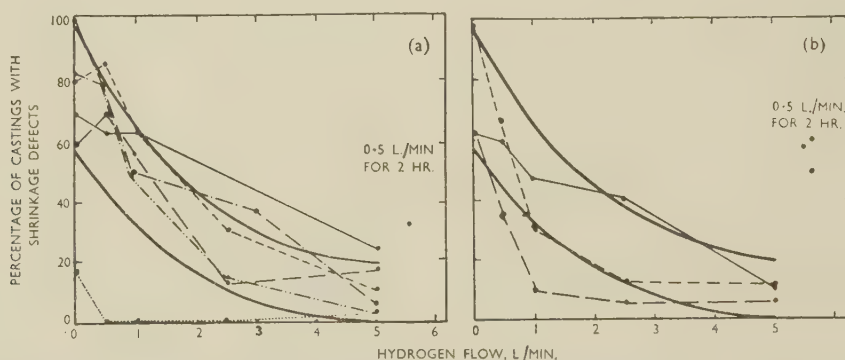


FIG. D2.—Percentage of Castings Showing Shrinkage Defects as a Function of Hydrogen Flow Rate. Ingot from (a) "poor" supply, (b) "good" supply (Laboratory Inspection Standards).

Dr. W. A. BAKER: I am glad that Dr. Scheuer has raised the question of the control of gas content, because I am convinced that in many castings a little gas is a good thing. It may be useful to outline the different technique which we have adopted. It will have been gathered that what Dr. Scheuer did was to take a bath of aluminium and bubble hydrogen through it. This produced a good deal of turbulence at the top, and the ingress of hydrogen was balanced against the egress through the turbulent surface, in order to arrive at a stable gas content.

We tackled the problem in a different way, by passing gas in through a tube projecting into the melt and shrouded by a hood, which need be only 2 in. in dia., and so occupies only a

in about the same time whether the melt is initially very gassy or substantially gas-free.

Dr. EMLEY (*in reply*): It has been questioned whether the fracture test for magnesium-zirconium alloys was carried out before the bulk of the metal was cast. That is invariably the case. Fig. D7 (Plate LXXVIII) shows fractured, 1-in.-dia. chill-cast bars of the binary magnesium-zirconium alloy, illustrating the difference in fracture appearance associated with satisfactory and marginal soluble zirconium contents. The commercial magnesium-zirconium alloys are actually somewhat finer grained than the binary alloy.

Dr. Baker has mentioned the desirability of being able to

\* E. Scheuer, S. J. Williams, and J. Wood, *Metal Ind.*, 1954, 85, 47, 63.

† E. Scheuer, S. J. Williams, and J. Wood, *ibid.*, 1950, 77, 235.



check the composition of a melt before pouring it. In that connection a quantometer is very useful, and particularly so to the ingot producer whose alloys contain expensive constituents such as thorium. Most of the major American magnesium foundries use quantometers to check the composition of the metal in large melting crucibles (1000–2000 lb.) before casting off into smaller pots, from which the castings are poured.

Mr. Payne's remarks about the possible effects of healed hot tears in the high-strength alloys containing rare-earth metals or thorium are very pertinent. With the thorium alloys there is an even greater radiographic difference in density between thorium and magnesium than there is between rare-earth metals and magnesium, so that fortunately the segregations in the case of the thorium alloys will be a good deal less serious than they look. It has been said that if these healed hot-tear types of segregation occurred in magnesium-aluminium alloys it would not be possible to detect them by radiography because of the small difference in radiographic density between aluminium and magnesium, and we have

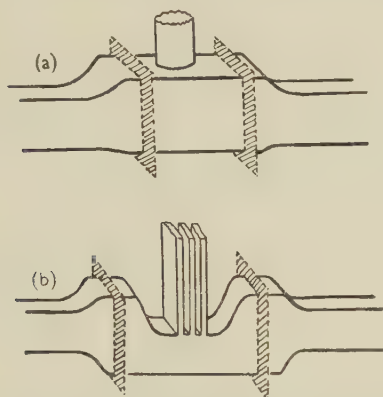


FIG. D8 (a)–(b).—Types of Enlarged Sprue Base Fitted with Perforated Metal Screens (shown hatched).

seen structures under the microscope which are undoubtedly of the healed hot-tear type in the magnesium-aluminium alloys.

Dr. Kondic has referred to the neglect of thermodynamics on the part of the authors of these papers, but I am not quite clear what he has in mind. So far as magnesium is concerned, thermodynamic considerations certainly govern the choice of salts used as fluxes for magnesium, the accidental introduction of impurities into the metal from these fluxes, and the possibility of using flux mixtures for removing certain trace impurities from the metal. Mould reaction, reaction with the atmosphere, &c., must, of course, proceed in the direction determined by the requirements of thermodynamics, but the extent to which these reactions occur will involve kinetic rather than thermodynamic considerations.

Regarding the subject of metal fluidity, a paper has very recently been published on the flow characteristics of some magnesium alloys.\*

The time taken to pour the mould can no doubt provide useful information. In one case my colleague Mr. Fisher noticed that the times of pouring a thin-walled casting varied by a factor of about 2. This casting frequently misran, and at his suggestion the arrangement of the sprue and screening device was changed from (a) to (b) in Fig. D8. When the change had been made, not only did the casting not

misrun, but it filled so fast that the metal shot out of the vent holes at the top of the casting to a height of several inches, indicating that what had happened before was that enough scum had been formed to block the screens.

I also hope that Dr. Kondic will enlarge on his interesting remarks about grain refinement. So far as magnesium alloys are concerned, there is one case where there is no doubt that nucleation provides the mechanism of grain refinement, namely, that of the magnesium-zirconium alloys. In the cast state these alloys show round zirconium-rich coring in the middle of the grains, and in the centres of these cores it is possible to etch up fine metallic particles, which appear to be zirconium.† The magnesium-zirconium system is a peritectic one, and the zirconium which separates has almost the same lattice parameters as magnesium and might therefore be expected to nucleate magnesium. In addition, it is possible in a partially solidified alloy to centrifuge out the zirconium cores, leaving a melt which solidifies with very coarse grain, despite a soluble zirconium content of 0.3–0.4%. Similarly, by setting up standing waves in a solidifying block of the alloy, it is possible to shake the zirconium cores into rhythmic layers, so that the solid block obtained shows alternate bands of fine and coarse grain.

Dr. Kondic wondered whether grain refinement is as desirable as it is sometimes made out to be. In all the magnesium-zirconium casting alloys, a high degree of grain refinement is necessary to achieve satisfactory tensile properties. It also suppresses any risk of cracking, both in casting and in welding, which some of these alloys might otherwise show. In the magnesium-aluminium-zinc alloys too, good tensile properties are dependent on adequate grain refinement.

Mr. M. H. FARMER,‡ B.Sc., A.I.M. (Member): I am not directly concerned with the manufacture of castings; my main concern is with their use. Looking at Mr. Fry's paper, I see that we do employ several of the methods which he suggests to detect faults in castings, but I should like to know how to assess the effect of the faults on serviceability. I have very seldom seen a perfect casting; most castings have minor faults. In the case of a valve used for liquid, if it does not leak on test, we know that it should give satisfactory service. On the other hand, we now use aluminium alloy castings under conditions of fatigue, and I should appreciate guidance on which defects we can accept in aluminium alloys and other materials intended for this purpose. No mention has been made of that aspect, but it is of particular concern to me.

Dr. B. LUNN,§ M.Sc., F.I.M. (Corresponding Member to the Council for Denmark): Mr. French mentions that temperature measurement is very important for the casting of copper-base alloys, and that it is difficult to attain good results. The best method, in my experience, is the quick-immersion technique with a high-grade quick-response recorder, but this is expensive, and many small foundries prefer to rely on a visual impression of the temperature of the melt, gained simply by looking at the surface of the metal. This visual method depends, of course, to a large extent on the impurities in the melt. It is known that large amounts of phosphorus will clear the surface to such an extent that we get a greater evolution of zinc fumes, giving the impression that the metal is at a higher temperature than is in fact the case, and in zinc-containing alloys sulphur has a similar effect. On p. 304 Mr. French mentions that the influence of sulphur in zinc-containing alloys is not clear. In such alloys sulphur will to some extent combine with the zinc, forming zinc sulphide with

\* J. E. Niesse, M. C. Flemings, and H. F. Taylor, *Trans. Amer. Found. Soc., Preprint*, 57–61, 1957.

† For a good example of a hexagonal core showing a central metallic particle see C. J. P. Ball, *J. Inst. Metals*, 1955–6, 84, 399 (Fig. 11, Plate LXVI).

‡ Metallurgist, The Associated Ethyl Co., Ltd., Ellesmere Port, Cheshire.

§ Technical Director, Nordiske Kabel- og Traadfabriker (Northern Cable and Wire Works), Copenhagen.

a rather high vapour pressure, and gun-metals with 0.1% sulphur will therefore show a considerably higher temperature to the foundryman than will alloys with less sulphur, so that he will tend to cast the alloys too cold, resulting in porosity which could have been avoided.

It is normal practice to assume that tin-bronzes should have a fairly high phosphorus content to give wear-resistant alloys when used under lubricated conditions with mineral oils, but I should like to point out that that advantage is not confined to tin-bronzes; it can apply even to brasses. During the latter part of the last war the Germans introduced a phosphorus-containing brass into their specifications (DIN 1726 SoGMS68). It was seldom used, because it is very difficult to cast owing to the high phosphorus content, but we have tested this unusual alloy in Copenhagen and found that the ability of the metal to form a protective film in the lubricated condition is very good. Wear-resistance does not depend

superintendent in this event, as some heats are expected to be rejected for high copper as well as some for low copper, is to minimize the scrap by aiming at a copper content in the middle of the specification limits. Usually this is not the best solution, and an optimal value can be arrived at in the following way.

The area under the distribution curve may be divided up as follows :

Area *A* represents the proportion of the heats with low copper requiring to be remelted;

Area *B* represents the proportion within specification;

Area *C* represents the proportion with high copper requiring to be remelted,

And  $A + B + C = 1$ .

A solution is required such that the cost of remelting the heats represented by  $A + C$  balances the saving in metal cost represented by having the billets represented by the area *B* at a lower mean copper content than the original mean  $M_1$ . It should be noted that  $M_2$  is the mean of the new displaced distribution and that area *B* has its own mean, which will be called  $T$ .

Knowing the mean  $M_1$ , the standard deviation of the distribution  $\sigma$ , and the limits  $O_A$  and  $O_B$ , the areas *A*, *B*, *C* may be calculated from standard statistical tables of the normal ordinate and integral.

If *N* heats are required within the limits  $O_A$  and  $O_B$  with an average copper content of  $T\%$ :

From the tables find the areas *A* and *C*,

for the lower limit look up  $x = \frac{(O_A - M_1)}{\sigma}$  for area *A*,

for the upper limit look up  $x = \frac{(O_B - M_1)}{\sigma}$  for area *C*.

The average copper content of the castings within the limits

$$O_A, O_B = T = M_1 + \frac{\sigma(O_A - O_B)}{B} = M_1 + \frac{\sigma(O_A - O_B)}{1 - A - C}.$$

If the cost of melting is £*W* per ton, the cost of zinc is £*Z* per ton, and the cost of copper is £*Z* + *D* per ton, then the total number of heats to be melted =  $N/B$ , and the total cost of the operation is the sum of the melting and metal costs, so that the average total cost for each acceptable heat produced

$$= \frac{\text{£}W}{B} + \frac{TD}{100} + Z.$$

This expression has to be minimized for variations in values of  $M_1$ . This is most readily solved by evaluation for various values of  $M_1$  and inspection of results for the minimum.

Turning to practical application, so far as the casting-shop superintendent is concerned a table showing the value of  $M_2$ , the mean copper content to be aimed at for all the castings so produced for various metal prices, casting cost, and standard deviation is required. Once established, casting costs will remain steady over a period of, say, three months, and individual metal price differences of less than £25 per ton will probably not be important. The standard deviation in this case will be the controlling factor and is subject to the greatest change, being dependent on the supply of scrap received.

Table A and Fig. D10 illustrate the movement of the desirable mean  $M_2$  for different values of the main variables. Such a table will be used by the casting-shop superintendent for fixing his target mean copper content.

The savings made per 100 tons of castings are shown in Table A (b), assuming that the normal target in this case is the mid-point of the specification, i.e. 63.0% copper. The

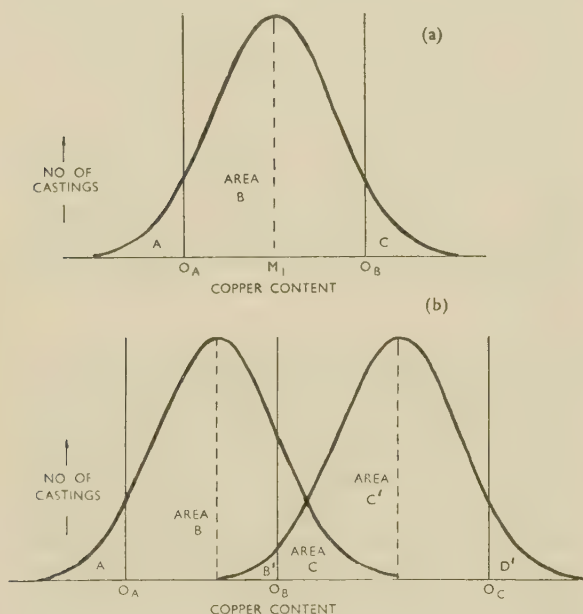


FIG. D9.

mainly on the hardness or structure of the metal, but much more on the chemical and physical properties of the surface.

Dr. R. KING,\* B.Sc., A.I.M. (Member): An illustration of the manner in which statistical methods can be used in the control of non-ferrous metal casting is contained in the following example. In this application, statistical analysis of routine results of chemical analysis is used to ensure that casting costs are kept under control. It is found in practice that the routine analysis results for heats weighed up to meet a particular specification can be represented conveniently by a normal distribution if taken over a relatively long period.

When a high-priced material such as copper is alloyed with a low-priced material such as zinc, two conditions apply which are worth consideration. These are illustrated in Fig. D9. The production of 70:30 brass is typified by (a), and the production of B.S. 265 and 266 together by (b).

The use of scrap, some of which may be purchased externally, has the effect of increasing the scatter of analysis results; hence the standard deviation of the normal curve tends to be large, and the points  $O_A$  and  $O_B$  are well covered by the curve. The natural tendency of the casting-shop

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decision as to what minimum savings are worth striving for depends on the individual foundry. £9 or £10 per 100 tons cast is probably the bottom limit, even though little continued effort is required to achieve this figure. The normal operating area will be around £50 per 100 tons of castings, and as such cannot be ignored.

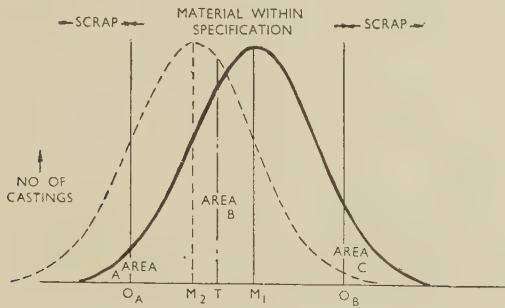


FIG. D10.

TABLE A (a).—Target Mean Percentage Copper Content ( $M_2$ ) for Various Values of Casting Cost, Standard Deviation, and Copper and Zinc Cost.

Zinc price taken as £98 per ton

Standard Deviation ( $\sigma$ )	Copper Price per Ton	Casting Cost per Heat				
		£2	£3	£4	£5	£6
$\pm 0.2\%$ Cu	£ 200	62.43	62.46	62.48	62.50	62.52
	240	62.40	62.43	62.46	62.48	62.49
	280	62.38	62.41	62.44	62.46	62.47
	320	62.36	62.40	62.42	62.44	62.46
$\pm 0.5\%$ Cu	200	62.82	62.88	62.91	62.92	62.94
	240	62.77	62.84	62.88	62.90	62.92
	280	62.72	62.80	62.85	62.87	62.89
	320	62.68	62.77	62.81	62.85	62.87

TABLE A (b).—Difference in Total Cost per 100 Tons of Castings, Using Target Means Given in Table A (a) Compared with a Mean of 63.0% Copper.

Standard Deviation ( $\sigma$ )	Copper Price per Ton	Casting Cost per Heat				
		£2	£3	£4	£5	£6
$\pm 0.2\%$ Cu	£ 200	50.1	47.2	45.2	43.7	42.4
	240	73.2	69.0	66.1	64.0	62.2
	280	97.1	91.7	88.0	85.1	82.8
	320	121.8	115.1	110.5	106.9	104.1
$\pm 0.5\%$ Cu	200	7.1	4.8	3.7	2.9	2.4
	240	13.1	9.1	6.9	5.6	4.7
	280	20.8	14.8	11.2	9.1	7.6
	320	29.7	21.3	16.5	13.4	11.3

Table A (b) illustrates the desirability of reducing the standard deviation as much as possible. In addition, it can be seen that the average total cost per ton is reduced considerably by a reduction in the standard deviation.

Thesecond example is a little more complex mathematically, but is based on the same principles. B.S. 265 and B.S. 266 for cold-rolled brass strip and sheet cover the ranges 61.5–64% copper and 64–67% copper, respectively. In practice, the

quantity of B.S. 266 required is usually small relative to that of B.S. 265, and its supply is often obtained from rejects for high copper from B.S. 265. A restriction of the lower copper limit to 62% to control the amount of  $\beta$  and make subsequent fabrication simpler is also commonly practised.

TABLE A (c).—Difference in Total Cost per 100 Tons Cast for 0.5% Standard Deviation Compared with 0.2% Standard Deviation.

Copper Cost per Ton	Casting Cost per Heat				
	£2	£3	£4	£5	£6
£ 200	£ 65	74	85	94	104
240	80	89	101	111	120
280	98	107	119	127	128
320	114	123	136	145	156

The situation is illustrated in Fig. D11. The problem revolves around finding the mean of the sums of the areas

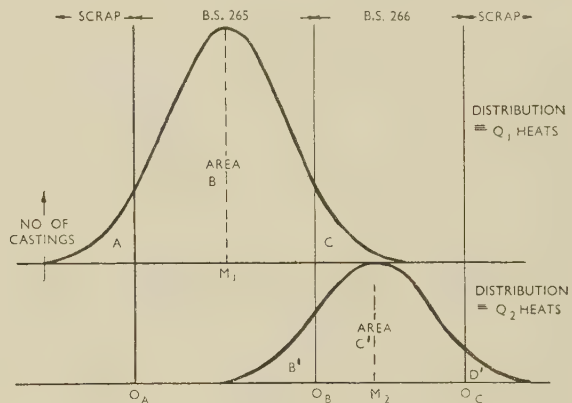


FIG. D11.

falling between the limits 62–64% copper and 64–67% copper and then minimizing the following total cost expression:

$$(Q_1 + Q_2)W + x \left( \frac{T_1 D}{100} + Z \right) + kx \left( \frac{T_2 D}{100} + Z \right)$$

for different values of  $M_1$  and  $M_2$ , where:

$x$  is the quantity of B.S. 265 required, and  $kx$  the quantity of B.S. 266.

$Q_1$  is the total amount of B.S. 265 cast.

$Q_2$  is the total amount of B.S. 266 cast.

$T_1$  is the mean copper content of the castings between the limits 62–67% copper.

$T_2$  is the mean copper content of the castings between the limits 64–66% copper.

$W$  is the melting cost.

$Z$  is the price of zinc.

$D + Z$  is the price of copper.

$M_1$  is the mean of the  $Q_1$  heats cast to B.S. 265.

$M_2$  is the mean of the  $Q_2$  heats cast to B.S. 266.

$\sigma$  is the standard deviation of the distributions, which is taken to be the same in both cases.

Coming to practical application, Table B gives an optimum scheme for values of  $M_1$  and  $M_2$  under stated conditions. This type of table would be compiled for use by the casting-shop superintendent. As before, the savings, though not spectacular, cannot be completely ignored. In the example

quoted, with a large standard deviation of 0.5% copper, they are of the order of £10 per 100 tons cast, and greater savings can be achieved, as in the previous example, by reducing the standard deviation to, say, 0.2 or 0.3% copper.

TABLE B.

Amount of Material to Melt	Target Mean, Cu%	Amount of B.S. 265	Amount of B.S. 266	Amount of Scrap Castings
tons		tons	tons	tons
104.09	62.8	97.54	0.85	5.70
11.62	64.4	2.46	9.15	0.01
		100.00	10.00	5.71

The price of copper is taken as £240 per ton, zinc as £98 per ton, and melting cost as 78s. 6d. per ton (typical metal prices for March 1957). The standard deviation is taken as 0.5% for both distributions. The savings are estimated at £9.88 for 100 tons cast.

Mr. G. B. EVANS,\* A.I.M., Assoc.I.Mech.E., A.F.R.Ae.S. (Member): Referring first to grain-size, two binary alloys of high strength are used in aircraft frame construction: aluminium-10% magnesium and aluminium-4% copper. The improvement of properties with grain-size in D.T.D. 304 is of particular interest just now, since some concern is felt about the behaviour of L53. Can the authors suggest whether this refinement of grain and the enhancement of properties, particularly elongation, and, possibly, improvement in other directions (such as in stress-corrosion-resistance) which may accompany it, is likely to be obtainable with future production castings in this alloy.

I would refer particularly to Mr. Fry's paper on non-destructive testing. As users, we are, of course, interested in obtaining sound castings as soon as possible and at the lowest cost. The two castings shown in Figs. D12-D16 (Plates LXXIX and LXXX) illustrate a variety of defects not dissimilar from those already discussed in the paper—in the first case cracks, and in the second porosity. Both these casting defects were detected by chromic acid anodizing at the customer's works.

The defects were very considerable in extent, and the castings are typical of 150 supplied to us during one month. The casting in Figs. D12-D13 exhibits cracks on either side of the lugs, and the second casting (Figs. D14-D16) shows porosity. These were supplied as Class 1 (aircraft) castings, and had passed the full radiographic requirements. We receive approximately 150 a month of a similar standard, and another 250 which have to be rectified for linear defects before use. The total production of which these form part is some 11,000 castings a month.

With magnesium-base alloy castings, the rejection rate is approximately 1½%, with a further 3-4% requiring rectification, from a consumption of some 5000 castings a month.

On the question of expense, it would seem that, broadly speaking, for radiography we pay 30-50% on the cost of the castings as delivered. Penetrant flaw detection involves 2s. 0d. per casting, which may represent as little as 1%, depending on the first cost of the casting. The cost of chromic acid anodizing is more difficult to assess, and this process has in any event to be carried out on light alloys for corrosion protection at present. We have compared chromic acid anodizing and other penetrant methods used on about 1000 castings a month for 3 months, without establishing any really significant differences in defect-finding efficiency.

Foundries have, in the past, employed X-ray examination for important castings: this detects many faults, but not all. As Mr. Fry says, other methods are available. Some found-

ries use them already. The aircraft industry would ask for yet greater emphasis on all possible methods which will ensure the delivery of sound castings. This might perhaps be improved by more attention to the quality of the first few castings made; even if this cost a little more and delayed the delivery of the first batch, it would prevent a great deal of trouble later.

The need for flaw detection is generally accepted for Class 1 castings, but one cannot ignore the other types of casting, of a more commercial quality, which in aircraft work are referred to as Class 3. These are not by normal requirements tested by X-ray. I think that there will be general agreement with Mr. Fry and others that cracks cannot be permitted to appear in a finished casting, even if the acceptable degree of porosity is debatable.

Cracks are usually connected with the surface, and this means that penetrants are applicable, although I do not wish to over-emphasize the importance of this method. To illustrate this point, a Class 3 casting, with typical defects revealed by penetrants at the customer's works, is shown in Figs. D17-D22 (Plates LXXX and LXXXI). If quality control does not prevent castings of this standard being produced, should not non-destructive flaw detection be used more widely?

Mr. MARTIN (*in reply*): Certainly the examples which Mr. Evans has shown us are frightening, but I feel that it would be as well to sound a note of warning. Radiography may fail to detect very fine porosity. Since layer porosity is most detrimental to the properties of castings, one is forced to supplement radiography with other tests, such as a fracture test. In the case of the aluminium-10% magnesium alloy, the porosity becomes darkened after heat-treatment and is easily identified.

On the question of chromic acid anodizing versus penetrants, I have always felt that chromic acid anodizing might offer an advantage because of the slight etching inherent in the process, but I have seen several cases in which lack of control of the anodizing process has produced effects similar to those demonstrated by Mr. Evans.

When porosity reaches the surface of a casting, penetrants afford a useful method of indicating those areas at which the fracture test should be applied.

I am not sure what improvement could be effected in D.T.D. 304 by further grain refinement, and I cannot offer any opinion regarding its effect on the stress-corrosion-resistance of the alloy. Grain refinement in this alloy helps to reduce hot shortness and to minimize the very fine hair-line contraction cracks which tend to develop and which are sometimes difficult to detect. Grain refining D.T.D. 304 alloy is not a straightforward effect of refining the primary phase. The object is to refine the particle size of the CuAl<sub>2</sub> phase in order to produce the highest elongation. The modification of B.S. L33 alloy provides a parallel case, because it is the silicon particles that are refined by the process and not the grain-size of the primary phase. A further example where "constituent refinement" is of importance is the hyper-eutectic silicon alloys in which the refinement is effected by phosphorus.

So far, no method of ensuring a fine silicon particle size in the 5% silicon alloys has been developed, and this would be a profitable field for investigation.

On the question of test-bars versus castings, I disagree violently with Mr. Hudson. If engineers are going to insist on a much higher standard of quality and much higher properties, we shall in effect be selling test-bars and not castings. In the case of Class 1 aircraft forgings, where the designer knows what minimum properties he must have, he marks on the drawing locations for the selection of sub-standard test-pieces. It is necessary to satisfy the designer,

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before supplying the forgings, that these minimum properties have in fact been met. I fail to see why a similar approach should not be made in the case of castings. The designer knows where his casting is to be stressed, and he can call for agreed minimum properties in the stressed areas. It will be a question of design coupled with casting technique to meet those minimum properties.

So far as test-bar castings themselves are concerned, I do not see that there is any argument on this point. In my paper I have set out what I consider to be the functions of a test-bar. If we accept these conditions, then the purpose of a tensile test-piece is clear. To confirm that a casting will be pressure-tight, you have to devise some other test.

I certainly think that too much attention is paid to gas content in the production of aluminium alloy castings, and this applies even where mechanical strength is important. In quite a number of cases in the production of melts of high-strength alloy, we have checked the properties of the metal as remelted and then checked them again after a conventional degassing treatment. In many cases the effect of the treatment is surprisingly small, and suggests that it is not gas content alone that affects the final properties. Very often the properties of the metal as remelted vary appreciably, and no amount of degassing will bring them up to the usually accepted level.

The use of a quantometer to check melts before casting would be ideal. When dealing with levels of alloying element such as 10% magnesium or 12% silicon, segregation in the sample becomes the overriding factor determining the accuracy of the result.

Mr. A. L. PENDREY,\* B.Sc. (Member): The direct-reading spectrograph is of great importance, because to make castings of a high standard requires metal of constant characteristics. If, for instance, the silicon content of the L33 alloy is 10%, one is dealing with quite a different alloy from that containing 13% silicon. By using the direct-reading spectrograph, it is possible to supply for gravity die-casting an alloy with a silicon content of  $10.5 \pm 0.3\%$ , and for sand casting one with a content of  $12.0 \pm 0.3\%$ , which will lead to better results.

The paper by Mr. Ruddle and Mr. Cibula is a logical successor to the paper published by the Institute of British Foundrymen on collaboration between the engineer and the foundryman,† since it is concerned with collaboration between the metallurgist and the foundryman. To my mind, the distribution of labour is that the Institute of Metals concentrates on alloys and their peculiarities and the I.B.F. on the mould. As regards gravity dies, there is a serious gap. The I.B.F. has always fostered the training of skilled moulders. Now we are mechanizing the process and introducing gravity dies and machine moulding, so that the work is becoming semi-skilled, and the man who actually puts the metal in the die no more than a labourer.

That is a serious drawback to producing satisfactory castings, and the I.B.F. should now endeavour to instruct the semi-skilled man in good casting practice. A pyrometer is generally provided in the foundry, but is often badly misused. We should get away from the portable indicator and employ a first-class potentiometer with electronic action, so that full scale is attained in  $1-1\frac{1}{2}$  sec., with a few sec. to reach temperature, and put this instrument in a good housing but ensure that it is clearly visible. More attention should be paid to the actual casting temperature and to the time elapsing before the metal is transferred from the container to the mould, and to the pouring time or speed, which brings us back to the man on the shop floor.

Mr. FISHER (*in reply*): I think the question of the strength of the actual casting is worthy of further exploration. First, however, I should like to reply to Mr. Hudson, who said earlier

that behaviour of the alloy in respect of the strength of the casting itself is apt to be disregarded in favour of its strength in a carefully selected test-bar. I would say, on behalf of the magnesium industry, that we have been for a very long time conscious of the fact that with a new alloy it is not sufficient to make a good test-bar; the alloy must make a good casting. I think it is true to say that modern alloy-development metallurgy goes far beyond the simple test-bar shape. Development at the laboratory stage includes the use of special shapes which will provide some information on the behaviour of a new alloy in the foundry. The laboratory with which I am associated makes a practice of developing an alloy, using such tests, until the stage is reached where we think that it is a good working possibility, and then we get some firms in the foundry industry to make typical castings with it, relying very much on their practical experience to determine whether it is in fact a good alloy or merely what is commonly known as a "test-bar alloy".

With regard to the strength of a casting, Mr. Hudson has made a point which I think is worth re-emphasis, namely, that what the user wants to know is the strength of the article which he is buying. He is not directly concerned with the strength of test-bars cut from that article, but merely uses them as a device to provide information which may otherwise be difficult to obtain.

The strength of a casting is a function of metallurgical quality and shape. The Institute is not directly concerned with the effect of shape, but, without wishing to appear a "metallurgical heretic", I wonder what is the relative importance of deviations from good metallurgical quality and of deviations from good shape?

Mr. Evans has shown some examples of castings which ought not to have been sold, but, on the other hand, how many potentially perfectly satisfactory castings have been scrapped because someone has found a defect and does not know whether or not it will affect the strength of the casting, and so plays safe and scraps the casting? That is probably the only correct course, but castings have to be made economically, and more information on the effect of such defects would, I am sure, help both the technical and the economic aspects of the problem.

On the question of specifications, I think that in this country, certainly for light alloys, the material specification calls for minimum mechanical properties based on separately cast test-bars, and, apart from a warning to users that the properties may not be attained in the casting, leaves it at that. However, the designer has to have data on which to base his calculations, and, lacking anything else, he takes the properties quoted in the specification and is frequently disappointed when he is told that they cannot be met in the actual casting. In the U.S.A. an attempt is made to alleviate this problem by specifying that test-bars cut from castings shall have 75% of the properties of separately cast test-bars, but I feel that this requirement is honoured in the spirit rather than in practice.

In Europe there has recently been an attempt to specify the actual strength of test-bars taken from castings. This raises rather a tricky problem. With magnesium-base alloys, casting sizes may vary from, say,  $\frac{1}{8}$  oz. in weight and  $\frac{1}{8}$  in. in section to over 400 lb. in weight and 3 in. in section. If one minimum tensile strength is chosen for all castings, it has to be low enough to include those of the thickest section, and at such a level the castings of thin section can be of very low quality and still pass the specification. If, on the other hand, a level of properties is chosen which is satisfactory for thin and small castings, the large ones will not have a chance of getting through.

It should be possible to overcome this difficulty by defining categories of castings by size and thickness of section and stating a level of properties for each, but is this the right

\* Chief Metallurgist, John Dale Ltd., London Colney, Herts. † G. Blanc and M. Jaumain, *Proc. Inst. Brit. Found.*, 1956, 49, B87.

method to adopt? It would require a great deal of work, and we should still be faced with the problem of only having information on a test-bar cut from the casting and be without information on the strength of the actual casting. At least one paper has been published in the U.S.A. in which the user, fortunately on rather a simple casting, examined various alloys and the products of various manufacturers by carrying out tests on the casting itself. Two important points arose. One was that the strongest test-bars did not come from the strongest castings. There are various factors to account for this, one being notch-sensitivity. There is also the point, made in this paper, that certain alloys, though capable of giving very strong castings, will not give such castings reproducibly. The user obviously prefers a slightly weaker alloy which is reproducible, to a stronger one which is not. That is another aspect of quality which has hardly been touched upon.

To sum up, what I think is required is work on actual cast shapes and perhaps, additionally, case histories of the strength of actual castings, giving where possible the effects of defects in those castings. If that information could be made public it would help designers, manufacturers, and everybody else concerned with castings.

Mr. WOOD (*in reply*): Dr. Kondic asked: "Why grain refine?" Tremendous reliance is placed commercially upon grain-size as measured by macro-sectioning or in many cases on etching the outside surface of the casting, and in the paper by Mr. Ruddell and Mr. Cibula a very good reason is given for fine grain in cast aluminium-4% copper alloy. It is clear that the tensile properties fall rapidly as the grain becomes coarser, and quite a fine grain-size is required for the castings to pass the relevant specification (Fig. 22, p. 287).

The story is not always as simple as that, however, as the following data illustrate. Test-pieces from the various sections of an 85 : 5 : 5 : 5 leaded gun-metal sand casting gave mean grain-sizes as follows:

Section thickness, in.	$\frac{1}{2}$	1	2	4
Mean grain dia., mm.	2	8	10	6

Ultimate tensile strength, ductility, and density, however, all showed a progressive change with change in section thickness, and there was no evidence of any discontinuity, comparable with the maximum in the grain-size/section-thickness relationship.

It would be interesting to extend this type of study to other alloys and to a wider range of casting conditions, and the additional data would be of value to those who have to interpret grain-size measurements.

Mr. FRENCH (*in reply*): I am glad that so much has been said about the strength of castings. Some speakers have been critical of the fact that the authors did not refer to this subject. It is a field which could well form the subject of a separate paper. Mr. Hudson (who referred to this matter) and I have been together on one or two committees where this subject has been discussed, and he will recall the immense amount of time given to the problem of how to tackle this question. It is a very big problem and a very important one, but I do not think it is one which could be included in the scope of this Symposium. That applies also to the question of mould materials, raised by Dr. Kondic.

Mr. Hudson has referred to quality of castings and mentioned some work he had been doing on step castings. He said that in the case of the 88 : 10 : 2 gun-metal the strength fell by 26% in going from 1-in. to 4-in. section, while with the 85 : 5 : 5 : 5 gun-metal there was a fall of about 50%. The difference he attributed to a difference in the soundness of the casting. I should like to ask whether density tests were carried out and whether a radiographic examination was made. Does it follow that the same technique will give the best

casting in 85 : 5 : 5 : 5 as in 88 : 10 : 2 gun-metal? I do not think so. It may be necessary to ensure the optimum casting technique for each alloy before making the comparison.

Dr. Kondic mentioned the three factors involved: the metal, the mould, and the human element. The old-fashioned foundryman had a great deal of "know-how", and the problem which now faces the industry is that we are losing the old skilled type of man and having to make do with men who are not highly skilled, who simply pour the metal into moulds. Those of us who are concerned with die-casting know that there is quite a knack in pouring metal into a die, and those of us who have worked on test-bars such as those of the I.B.F. type are aware that there is usually one moulder in the shop who can pour from the same pot, a much better test-bar than the others because he has the knack of putting the metal into the mould. The metallurgist must find out how to use the relatively unskilled man to achieve the same result as that obtained by the skilled man. That is where we hope that the B.N.F. work on gating methods will be of considerable help.

Dr. Kondic asked about the influence of aluminium on the fluidity of brasses. Mr. Cibula has said that fluidity is measured in the foundry by the ability of a metal to run through small spaces and to fill corners. My answer to Dr. Kondic is fundamentally that if we try to cast brass containing no aluminium into a die, it does not run through a small section or into corners. An explanation is presumably to be found in the deoxidizing effect of aluminium on the skin-forming characteristics of brass.

With regard to the Pfeiffer test for gas determination, I cannot speak from experience of aluminium alloys, but it works with aluminium bronzes, and if a whole series of tests is made with metal in the same condition, consistent results will be obtained. That is what matters to the foundryman and the man using this test on the shop floor. If a gas content of more than a certain amount is shown at a given level of pressure, scrap castings may be expected.

Dr. Lunn referred to temperature control and to the use of high-quality equipment. I am not sure that he appreciates one of the major issues for the copper-alloy metallurgist, namely, the fact that it is the tip end which fails so quickly and leads to so much inconsistency.

He mentioned the influence of sulphur, which is also of great interest, because sulphur is becoming a problem in view of the low-grade fuel oils which have to be used—low grade, that is, with regard to sulphur content. It is interesting to find that sulphur has such a profound effect on gun-metals, because in these days of secondary origin they are frequently of very high sulphur content.

Mr. Wood gave some results on the relation between the properties of gun-metals and the grain-size and quoted section thicknesses of  $\frac{1}{2}$ , 1, 2, and 4 in. Do these relate to the same tests as those to which Mr. Hudson referred? I hope that the full results of these tests will be made available in the near future.

Dr. V. KONDIC: I have been asked to amplify two points. Mr. Cibula referred to fluidity and to the spiral test. It is well known that an effective method of raising the fluidity of cast iron is to increase the phosphorus content, but phosphorus has no effect on the results obtained by the spiral test. This shows that the spiral test does not measure the ability of an alloy to fill the mould, which is what matters in founding.

I was also asked what I had in mind by my reference to thermodynamics. When the metal is put into a pot, a great many things can happen to it. There is no better way of summarizing these reactions than by looking at them from the point of view of chemical thermodynamics.

On the question of grain-size, my suggestion is that nucleation is not the factor responsible for the grain-size of a casting. If it is asserted that particles such as carbides or



borides or nitrides are responsible for the grain-size of aluminium castings—the field with which we are most familiar—it is possible to produce evidence that, using the same alloy, one can produce a range of grain-sizes without otherwise changing the alloy at all. I cannot believe, therefore, that it is simply nucleation which is responsible for the final grain-size in castings. I believe that titanium exerts some influence in aluminium alloys, but at present the nucleation theory raises serious doubts in my mind about the ultimate origin of cast grain-size.

Dr. W. M. DOYLE,\* M.Eng., F.I.M. (Member): I should like to see the excellent paper by Mr. Ruddle and Mr. Cibula rewritten in a simple form and circulated to as many practical foundrymen as possible. This review of the theoretical aspects of running, gating, flow of metal, and elimination of defects in castings is most valuable, and it would be a great pity if the foundrymen responsible for the practical application of these principles were to be discouraged by the mathematical treatment of some of the procedures. A simplified version of the paper could well form part of the education and further training of foundry foremen.

Many detailed figures are given in this paper for ratios and sizes of gates, sprues, risers, &c. In Table II, is it implied that the ratios shown apply to all types of aluminium alloy? I would question the statement on p. 288 that grain coarsening occurs in aluminium alloys containing grain refiners if the melt is heated above 700°C. I agree that this tendency exists in the case of the D.T.D. 300 and D.T.D. 304 types of alloy, but is it true of all aluminium alloys?

The paper by Mr. Martin is a very good one for statisticians and research workers, who are sometimes envied by routine foundry metallurgists. It would be interesting to know whether or not the author uses these complete methods of statistical analysis in his own routine foundry.

On the basis of the discussion there seems to be tacit agreement that, despite the controls which can be put on quality, we cannot prevent Class 3 castings masquerading as Class 1. I should like to ask foundrymen just what they think. Can they or can they not control their product? There is a definite need for charts and graphs showing the trends in the various factors affecting inspection, for example, chemical composition, tensile properties, and so on.

On p. 223 Mr. Martin lists some of the disadvantages of sampling batches on the basis of the acceptance of a defect-free sample. These are very significant, because if the customer is likely to receive a high proportion of batches containing two or more defective castings, as stated, then a method of sampling which may lead to the rejection by the producer of batches containing only one defective casting is surely inadvisable and uneconomic, particularly if such batches form as much as 19% of the total.

One minor criticism of the paper by Mr. Carless is that his statements are to a great extent applicable only to sand castings, and he does not indicate that die-castings may involve different procedures. I agree with his suggestion (p. 229) that runners and risers should be identified, but hardly by the use of fast-drying paint, because there is always a danger of a change in colour with temperature. A very good method is to include the alloy designation as an insert in the mould or die. This obviates the need for the operator to spend time in painting and also reduces the difficulties attending colour changes and the ever-present danger of faulty identification.

For spectrographic analysis we have found it very satisfactory to cast test specimens incorporating a number of  $\frac{1}{4}$ -in.-dia. "pencils", subsequently used as electrodes in the spark unit. In this way the cutting and milling of the rectangular cast slabs suggested by Mr. Carless are eliminated. We do not regard such slabs as satisfactory specimens for

spectrographic analysis. We are developing the use of the Hilger direct-reading attachment to the spectrograph for foundry control, and can obtain a complete analysis in 3 min., using the pencil type of specimen.

The author discusses hexachlorethane tablets for degassing, but does not mention chlorine or nitrogen. A reference to these gases is made in the paper by Mr. Ruddle and Mr. Cibula. In employing degassing tablets, fluxes, &c., there is considerable danger of hydrogen pick-up from these salts. The B.N.F. reduced-pressure test, when used alone, has a number of disadvantages, and we believe that the Telegas apparatus developed by Dr. Ransley should be employed in conjunction with the reduced-pressure-test equipment. At the moment we are not getting correlatable results with the Telegas instrument compared with the vacuum-extraction method, but we feel that it is only a question of time before this instrument is in routine use in the foundry.

Mr. Carless appears to ignore the use of gas-generating powder or gas injection, now commonly applied in the production of certain commercial die-castings which form an essential part of the production of a general die foundry. Dr. Scheuer has outlined some of the advantages of this procedure. It seems, on the face of it, to be not quite respectable to do this sort of thing, but such methods are justified, because they help to improve the fluidity of the metal, or its apparent fluidity, and also reduce the shrinkage porosity. In addition, with commercial die-castings, in which gas may be deliberately added to metal (which, of course, is free from magnesium or zinc), insistence on a casting temperature of less than 800°C. is no longer fundamentally necessary. If a lower rejection rate is obtained when die-castings are produced with metal at a temperature greater than 800°C., there is no justification for insisting that the temperature should be controlled at a lower level.

I agree, however, that in the case of sand castings the design of the runner and riser systems should be such that a considerably lower temperature can be used. I should like to have the opinion of Mr. Carless on where the metallurgical control ends and where the production control takes over, because I do not entirely agree with the statement made on the last page of his paper, to the effect that the laboratory should confirm the efficiency of the procedures and record the trends. This is not the limit of the metallurgist's responsibility; he should actually control technically the production of satisfactory castings.

I would suggest that the factors governing the control of impurities, such as iron, in magnesium-base alloys should be treated more extensively than they are by Dr. Emley and Mr. Fisher on p. 240 of their paper. On p. 247 these authors make a brief comment on the appearance of the blue surface mottling and state that it is of little practical significance. I agree with Mr. Payne's statement that this mottling may be associated with areas of general porosity and coarse grain immediately below the surface.

I now come to the thorny question of the designer of castings linking up with the foundryman. In forgings, of which my company has a very wide experience, relations with the designer are quite close, and we have drawn up a series of minimum design data and guarantee the properties in the various directions in any important forging which we make. All that the designer has to do is to specify where he would like the grain flow to occur, and if this is not possible, we agree on a compromise. Such a procedure is not practicable in the case of castings, and the only way of implementing Mr. Hudson's point is to try the actual casting out on a test-bed. This may not be as uneconomic as it sounds, because one major firm in this country adopts this procedure. Some designers will support the statement on p. 251 that more information is required on the effect of casting defects on mechanical properties, and particularly on creep and fatigue.

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They would like to have these data for all alloys, and not only for those based on magnesium. Most users will, however, adopt the attitude that the foundryman should be able to eliminate these defects by proper metallurgical control.

There is sound common sense in the statements made in Sections 3 and 4 (p. 253), which represent the ideal conditions for the control of development work and the standardization of production techniques. Unfortunately, economics of necessity play an important part in foundry management, and it is only very large foundries which can adopt these ideal conditions.

With regard to the aluminium alloys used in pressure die-casting, we have always found it desirable to modify the LM6 type of alloy, despite the severe chilling and resulting modification from the actual pressure die-casting process. Mr. Sharp does not mention LM24, which is becoming very popular for commercial work. This specification permits a higher iron content than LM2, so that castings can be produced with a better surface finish, since a lighter grade of lubricant may be used. The author makes no mention of the lubricants used in pressure die-casting, but we consider these to be very important. In our experience it is necessary to adjust the lubricant according to the casting. A difficult casting may require a heavy lubricant, such as aluminium powder in a mineral oil, whereas with a simpler casting or an easier alloy colloidal graphite in water is adequate.

The most valuable part of Mr. Sharp's paper is that concerned with the relationship between speed of metal flow and the time of filling the die, in that it provides a basis for a theoretical determination of the best conditions for pressure die-casting. It is a pity that at the same time the author does not consider the effects of die temperature.

In the paper by Mr. Fry on non-destructive testing, I cannot agree with the statement in Section VIII. 2 (p. 364) that: "Gas porosity, unless very severe, does not reduce the mechanical properties appreciably." I would refer him to curves A and B in Fig. 18 (p. 284) of the paper by Mr. Ruddle and Mr. Cibula. Gas porosity can also cause a considerable fall in elongation, and pressure-tightness may not be achieved. Mr. Fry states that: "This type of defect can be successfully treated by impregnation", but this is not always permissible. Mr. Fry does not consider the dense inclusions in Fig. 27 (Plate LXI) to be serious. He states that the defect in Fig. 29 (Plate LXII) is not detectable by penetrant flaw examination. Am I right in interpreting this to mean that radiography is the more discriminating way of finding such defects? In certain cases a dye penetrant will reveal defects not shown by radiography, and vice versa, so that the two methods should be considered as complementary. It is rare for a casting to be made which is absolutely perfect, and acceptance or rejection may be at the discretion of the radiologist, who should make his decision in the light of the end use of the casting. For this reason the paper would be considerably improved, as Mr. Farmer has suggested, if Mr. Fry gave some general indication of what, in his opinion, are the permissible levels of the various defects.

Mr. CIBULA (*in reply*): Several contributors have raised the question of when grain refinement is beneficial. Grain-size is, of course, only one of the factors which control the properties of a casting, and if some other factor has a greater effect on the property in which one is interested, obviously grain refinement may cause little improvement. For example, the aluminium-copper-silicon alloy LM4 contains large quantities of brittle intermetallic constituents which are insoluble and limit the tensile properties of the casting, and grain-size has little or no influence on the strength of the alloy because it does not affect the crystallization of the intermetallic compounds; the grain-size has a pronounced influence on hot-tearing, on the other hand, as this property is not affected by the presence of intermetallic constituents. In contrast, grain refinement improves both tensile properties

and hot-tearing resistance in LM11 alloy (aluminium-4½% copper) from which excessive amounts of insoluble intermetallic constituents are deliberately excluded.

The variation of properties with section thickness in a gun-metal step casting, described by Mr. Wood, may have been due to a change in the form of the porosity as the rate of freezing fell, this effect masking any influence of the associated change in grain-size. Incidentally, in gun-metal castings the highest tensile properties are obtained when the grain structure is columnar, as equiaxial structures, particularly of large grain-size, are associated with deleterious forms of shrinkage porosity.

Grain coarsening in aluminium alloy castings becomes appreciable when the metal is heated above 700° C. and is very pronounced if the temperature is allowed to rise to 800° C. This tendency may vary to some extent from one aluminium alloy to another, as the grain-sizes obtainable depend on the constitution of the alloy; however, there is no information on whether the grain-refining nuclei, the solution of which is the chief cause of grain coarsening, are more soluble in some alloys than in others.

The gating ratios recommended for running and gating systems for aluminium alloys are all high, unchoked systems having been found most satisfactory for cross-forming alloys. There is probably little justification for differentiating between one aluminium alloy and another in selecting a gating ratio, even though alloys containing magnesium are more liable to cross formation.

Mr. MARTIN (*in reply*): I am a little disappointed at Dr. Doyle's statement that he considers my paper of interest only to statisticians and research workers, particularly since I am neither a statistician nor a research worker. I have tried to demonstrate the usefulness of organizing available information in the simplest possible terms and seeing what can be got out of it. Illustrations indicating where statistical methods are definitely not applicable are as important as illustrations demonstrating their applications. We use simple charts to keep track of melt compositions and tensile properties. Motor-car piston castings are dealt with on the lines outlined in the paper, and the example of the strength tests on the gravity die-cast bracket given is an actual example.

I think that this latter example emphasizes the importance of the method of loading the casting, which is just as important as ensuring that there is adequate strength in the casting itself.

I admit that sampling is difficult to apply so far as castings are concerned. Visual examination and dimensional checks do not necessarily lend themselves to sampling treatment. It would be useful to be able to use sampling methods effectively in cases where destructive tests cause the rejection of each component selected for test. Unfortunately, customers machining small components usually expect a rate of rejection not greater than 3%, though some may accept 5%, and to guarantee this level would involve very large samples indeed and would not be economic. When dealing with similar castings produced from one alloy, it is possible to devise a sampling system to control the alloy quality in general terms and then to treat individual items on a different basis.

Sequential sampling techniques offer some assistance and ensure the use of the absolute minimum of material in establishing whether the day's production is good or bad. As the sample size increases, it offers a more and more convincing case for accepting or rejecting the day's work at the completion of the test. By contrast, one frequently meets sampling schemes in which a day's production of castings is grouped in batches of 50 or 100 and a casting is selected from each batch and tested. If the sample is acceptable, the batch is released; if it is rejected, the batch is scrapped. Such a procedure gives the customer no protection whatever.

Admittedly, the significance tests and correlation techniques described are research tools rather than control



techniques. The direct application of statistical methods to the control of the quality of castings is severely limited. I thought it justifiable to include reference to these research methods, to warn founders against accepting the results of elementary work without criticism.

Mr. SHARP (*in reply*): With regard to Dr. Doyle's comments, I have never found it necessary to modify LM6 before pressure casting, although my experience has been limited to fairly light sections, say, of the order of  $\frac{3}{8}$  in. I can well visualize that with heavier sections some modification would be desirable. I do not see, however, how such modification could be easily accomplished in practice in a pressure foundry, where the molten alloy is usually kept in a holding furnace for prolonged periods. As I understand it, the effects of modification pass off when the metal is held in the molten condition for any length of time.

I did not deal in my paper with the use of lubricants because I feel that this is a field full of fads and fancies. We started investigations mainly with the intention of eliminating the use of graphite in its various forms, because this substance is messy and dirty. We found, however, that we were unable to dispense with it. We made experiments with aluminium powder in a carrier such as paraffin, and with paraffin alone, as well as with various proprietary lubricants and oils. While many of these have their uses, they also have their drawbacks. The overall conclusion has been reached that, given a reasonable casting design and die design, as well as a controlled maintenance programme, so as to ensure freedom from drags, and with a reasonable uniformity of die temperature, it is possible to operate with a spray of paraffin alone. (Moving parts of the die have, of course, to be oiled separately.) This situation never seems to last for long, however, even with an ideal die. Sooner or later movement or distortion of the die occurs, and sticking of the casting in the die and the beginnings of a drag ensue. It is usually not possible, because of production commitments, to take the die out at once; it is therefore necessary to start using a lubricant with high-temperature properties. The only material to meet the requirements is some form of graphite, so we are back where we started.

Some data are available, on die temperatures, but they were not included because they appear to fall in line with the other factors. Thus, if suitable conditions of flow through the gate into the cavity prevail and there is suitable section uniformity, the temperature distribution in the die is fairly uniform, allowing for some correction by the distribution of water-cooling lines. Where by reason of poor design, or of the necessities of the design, these conditions cannot be attained, the die temperature never falls into line; there is a large variation throughout the cavity, and consequent production difficulties arise which have to be put up with in order to produce the design.

To quote figures, where we attain something reasonably near the optimum speed of flow through the gate and cavity-filling time, the die temperature settles down at about 250°–350° F. (120°–175° C.). That is the temperature shown for the casting faces of the die by a contact pyrometer of good sensitivity immediately on opening the die and ejecting the casting. Where adverse conditions prevail, it will be found that certain parts of the cavities run up to 600°–700° F. (310°–370° C.) when checked in a similar way.

Mr. CARLESS (*in reply*): With reference to Dr. Doyle's point regarding identification by painting; touching the runners and risers with paints of different colours is much more convenient than stamping; the colour can be seen at a distance and the scrap returned to the various storage bins is easily identified. That heat may destroy the colour is evident, but the castings are not painted while they are so

hot that this will happen, and the colour is destroyed only when the material is put back into the melting pot.

I agree with Dr. Doyle that my treatment of the subject of die-casting has been perhaps a little cavalier. It is true that the slightly "non-respectable" practice, as he calls it, of deliberately gassing certain melts for die-cast work is in common use. We do not employ it any more than we are obliged, but in certain cases it is necessary to control local shrinkage by this means. The limiting temperatures given in the paper refer expressly to sand-cast work.

On the question of degassing, we have tried chlorine and find it very effective, but it is not a nice gas with which to work, and we find hexachlorethane tablets consistently convenient. With reasonable care, no trouble arises from hygroscopy or deliquescence. Nitrogen is used on occasion and has been for many years. It is an effective degassing agent.

Another question which Dr. Doyle raises is that of the spectrographic sample. This is always a debatable point, but the pencil type of specimen has not proved very satisfactory, in our work at any rate. We are at the moment experimenting with the disc type. Dr. Doyle's conditions, however, probably differ from ours. We are satisfied at the moment with determining comparatively small amounts of elements and have not attempted to deal with major constituents, such as 10% magnesium in LM10 or anything of that order.

The question of where the metallurgist's responsibilities end and official inspection takes over is, I consider, one of purely local arrangement. In our firm the metallurgist works with the Inspector all the way through, but his control does not extend to dimensional and similar final checks.

Dr. EMLEY (*in reply*): Dr. Doyle would have liked our paper to say more on the control of iron content in high-purity magnesium-aluminium alloys. The paper was written from the point of view of the founder who makes up melts from approved ingot and his own high-purity scrap; we felt that the methods by which the ingot producer made the high-purity alloy ingot in the first case fell outside the intended scope of the Symposium. It is perhaps worth adding that chromium-manganese-aluminium steel crucibles behave like "well-seasoned" mild-steel crucibles as regards iron pick-up, so that the founder does not need to be so careful in avoiding overheating of melts as when he is melting in mild steel.

Dr. Kondic has explained that what he had in mind in suggesting that some reference in the papers to the thermodynamic approach might have been interesting was what can happen to a charge of metal when it is put in a crucible and heated. Where magnesium is concerned, the teaching of thermodynamics is that it will be converted completely into a mixture of MgO and Mg<sub>3</sub>N<sub>2</sub>.

Mr. L. A. J. LODDER, B.Sc., A.R.C.S.\*: I should like to comment on Mr. Sharp's paper from the point of view of zinc alloy die-castings.

Mr. Sharp describes die-casting machines but concentrates mainly on the cold-chamber machines used for aluminium alloys. He refers correctly to the plunger-operated hot-chamber machine for casting zinc alloys, but states that it is operated at a pressure of 500 lb./in.<sup>2</sup>. In fact, the optimum pressure for casting zinc alloys is about 1500 lb./in.<sup>2</sup>, and this is customarily attained and even exceeded in practice. The lower pressure refers to the older, virtually obsolete, direct-air machines.

According to the extent to which it can be mechanized, pressure die-casting in general lends itself to a measure of control over some of the casting variables which have been discussed in relation to other methods of casting. In the case of the hot-chamber machine, in particular, transfer of

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metal is avoided and, as Mr. Sharp mentions, rapidity of production is attained. This in turn assists in control over die temperature.

The paper suggests that the analysis of zinc alloys—so essential to assure freedom from contamination—is a difficult procedure. In fact, techniques described in B.S. 1225, which incidentally make use of cast pencils 8 mm. in dia., have been used satisfactorily for a number of years by the larger die-casters in this country. Admittedly, they involve the expense of spectrographic equipment and trained personnel. However, there is now a British Standard Certification Mark Scheme for zinc alloy die-castings, and licencees, who must use the "Kite" mark on their products, undertake to analyse, or to have analysed, samples of their production on a regular basis. This to a considerable extent solves the problem for the smaller die-caster, who can now take advantage of a service operated by a communal laboratory with results made available within 24 hr., or less if contamination is present.

As to the design aspect of die-castings, I would confirm that a mere replica of a component produced in an alternative material by an alternative method is seldom satisfactory. Some of the more straightforward principles of design for zinc alloy die-castings are covered in British Standard Code of Practice 3001. This deals also with casting practice and stresses the need for continuous co-operation between the die-caster and customer on design aspects.

The "steam test", as Mr. Sharp states, constituted a 10-day delay on the release of castings. It probably had some value in the days before the Certification Scheme, and in the absence of analytical facilities would serve to pick out heavily contaminated castings on the basis of visual examination for distortion. It carried a dimensional clause to the effect that expansion in the course of the test should not exceed 0.001 in./in. and this could serve as a basis for rejection. In fact, this stipulation has been found to be unsound in principle. The growth associated with corrosion induced in the steam test is superficial and unrelated to the length of measurement, but 10 days in an atmosphere at 95° C. causes freshly cast zinc alloy die-castings to shrink slightly and older ones to expand slightly, owing to phase changes. Both these dimensional changes are related to length of measurement, one diminishing and the other supplementing the expansion due to the surface effect. In fact, with fresh or with older castings the longer the length of measurement, the better the prospect of meeting the steam-test dimensional stipulation. Indeed, new castings free from contamination and measured over a sufficient length could show an overall contraction. The inaccuracy of the test is such that it has now been deleted from the revised version of B.S. 1004.

In connection with the recent revision of B.S. 1004, I should like to correct Mr. Sharp in his reference to zinc alloys in ingot form. The magnesium content of ingot alloy is now 0.04–0.06%, though it remains at 0.03–0.06% in the case of castings. The die-caster is also allowed small tolerances for the harmful impurities lead, cadmium, and tin, and also for iron and copper, and for the alloying element aluminium at the lower end of its permitted range.

Mr. W. E. DUCKWORTH,\* M.A., A.I.M., A.I.S.: I should like to join with Mr. Martin in urging that statistical methods are not merely a tool for the research worker but are also useful to the practical foundryman. We are employing them in our own foundry and find them extremely helpful. There is one difficulty which we have found in persuading metallurgists to use statistics, and that is that statistics involve mathematics. Even the simplest statistical test seems to them to involve fearsome-looking graphs and the use of formulæ such as those given on p. 214 of Mr. Martin's paper. It is understandable, therefore, that the man on the foundry floor tends to regard it all as high-falutin' mumbo-jumbo.

To overcome this problem, and to make it easier to use statistical methods without a calculating machine, we have been developing, along with others, some extremely simple tests of significance which can be applied on the spot, on the factory floor, or in the metallurgist's office. These tests do not involve any arithmetic.

I should like to give an example of the kind of test employed. Suppose that two sets of results are available, let us say for the tensile test on two unspecified alloys, *A* and *B*. The figures are as follows:

Alloy <i>A</i>		Alloy <i>B</i>	
9.5	10.4	9.4	11.1
9.1	11.5	9.6	9.4
9.0	11.2	9.2	11.4
9.5	11.6	8.0	10.9
12.2	10.2	8.9	11.3
10.0	11.8	8.5	9.8
10.7	12.0	9.7	9.3

With results of that order, it is often difficult to say offhand whether or not the strength of alloy *A* is higher than that of alloy *B*. The method to apply is to find the highest observa-



FIG. D23.

tion and the lowest observation in each group. For *A* the highest observation is 12.2 and the lowest is 9.0. For *B* the highest observation is 11.4 and the lowest is 8.0. We then find the number of observations in the *A* group which are higher than the highest in the *B* group. (It is obvious that the highest and lowest figures of the *A* group are higher than those of the *B* group.) In the *A* group there are five observations (12.0, 11.8, 11.6, 11.5, and 12.2) higher than the highest observation in the *B* group. There are also three observations in the *B* group (8.0, 8.9, 8.5) lower than the lowest observation in the *A* group. We add the 5 and 3 and get a score of 8.

Professor Tukey of Princeton University has worked out that if the score is equal to or greater than 7 it can be said that the difference is 5% significant, while if the score is equal to or greater than 10 it is 1% significant, and if it is equal to or greater than 14, it is 0.1% significant. The score in the example chosen is 8, so that it is 5% significant. The actual *t* test with this example shows a significance level of 4%, which is near enough. That constitutes an extremely easy test, which can be applied on the shop floor.

We are often interested in a correlation. For instance, one may want to see the effect of grain-size on the tensile strength; for a particular alloy, it may be desired to determine whether or not grain-size has any effect on the tensile strength. A considerable scatter of results, may be obtained, as in Fig. D23.

There is an example of this sort of thing on p. 225 of Mr. Martin's paper. A statistician can carry out a complicated

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calculation called a regression analysis, and he may ultimately say: "There is something in it." However, in three minutes, by a simple process of counting and a small adding-up operation, one can decide that for oneself.

Let us suppose that there are 16 observations. A horizontal line is drawn which divides them in half, so that there are 8 above it and 8 below it. A vertical line is also drawn to divide them in half, so that there are 8 to the left of it and 8 to the right of it. The graph is then as illustrated in Fig. D24. One then places a ruler horizontally and starts moving



Fig. D24.

downwards from the top, counting the number of observations in the top-right quadrant, before an observation occurs in the top-left quadrant. In Fig. D24 there are 5. The ruler is then placed vertically and moved from right to left and the number is counted of observations in the top-right quadrant before coming to an observation in the bottom-right quadrant; in this example there are 2. A similar procedure is then applied to the two lower quadrants and the two left-hand quadrants, and it is found that the total comes to 14. It has been worked out that, with a score equal to or greater than 11, the correlation is 5% significant; if it is equal to or greater than 14, it is 1% significant; and if it is equal to or greater than 18, it is 0.1% significant.

These are two tests which even metallurgists should be able to employ!

Mr. E. ELLIOTT,\* A.Met., F.I.M. (Member): Mr. Sharp says on p. 332 that an LM5 alloy pressure die-casting "may be anodized or polished to a white finish". LM5 is an aluminium-3-6% magnesium binary alloy. I agree that pressure die-castings in this alloy can be polished to a very good finish indeed, but to anodize them tends to show up the flow lines, thereby spoiling the appearance. There is a demand for pressure die-castings which can be polished and given a sufficiently thick anodized coating to afford good protection, and the result should be attractive. Work is being carried out mainly, I believe, on aluminium-7% magnesium alloys, special attention being paid to die design. This is a question of quality control, despite the fact that it concerns the mould, which I understand is not within the scope of this Symposium. Perhaps Mr. Sharp would like to comment on this point.

It has been said that although an excellent tool exists for improving the properties of the aluminium-12% silicon alloy in the shape of the modification method, there is no corresponding process for the aluminium-5% silicon alloy, and that it would be very advantageous to have one. Recently I saw in an American journal a reference to a casting alloy of high strength designated 42B. Further details from the manu-

facturers included very specific claims as to the properties obtained, but the information about how it was done was rather more vague. The alloy is of the American 356 type (aluminium-7% silicon-0.3% magnesium) and similar to LM8, which is an aluminium-5% silicon-0.5% magnesium alloy. The claims for properties included higher strength than LM8-WP, combined with better ductility. It was stated that the alloy was not high-purity-base, and that the properties were obtained by the addition of certain elements, including beryllium and sodium. Might this be regarded as a modification method for a hypoeutectic aluminium-silicon alloy?

Mr. SHARP (*in reply*): I agree with Mr. Elliott that the anodizing of LM5 pressure die-castings is at present limited to relatively small and simple components. Work is still going on to try to extend the field.

The bias in my paper is, of course, largely towards aluminium pressure die-castings. I would support strongly Mr. Lodder's remarks regarding the use of hot-chamber machines for zinc castings and the very interesting possibilities for producing fully automatic pressure die-castings in zinc alloys with hot-chamber machines.

Following on a remark by Mr. Carless on a point touched upon by Dr. Doyle in relation to the responsibility for quality control of the metallurgist and of the foundry supervisor, the way in which I view this is that the activities of a company are the ultimate responsibility of the board of directors. The activities of the production unit, whether a machine shop or a foundry, are obviously the responsibility, under the board, of the production superintendent or foundry superintendent. The quality-control aspect is taken care of by the quality-control or inspection department. It is usual, and I think a very good thing, that the chains of responsibility on the production and the quality-control side are separate and join only at a fairly high level.

We have been discussing in these papers quality control involving the use of test methods and test equipment. The personnel needed to operate such equipment and to carry out the observations and make the reports on the quality-control side will depend on the techniques and the methods. We may need people to take dimensions. Probably they would be regarded as being in the engineering rather than the metallurgical field. The people who carry out the analyses are probably not metallurgists but chemists, or, if spectrographic analysis is involved, they may be physicists. It is surely stretching the imagination to call the man who takes routine temperature checks a metallurgist. The main techniques of production quality control are now being broken down to fairly simple unit operations, even though they may involve complex equipment, and the actual operations and observations are being carried out more and more by semi-skilled operatives who form the personnel of the inspection department, whilst the metallurgist as such is perhaps being confined more and more to the research division.

Mr. D. W. BROWN:† Instrumentation in the non-ferrous foundry must be an important factor in the control of quality. The average non-ferrous foundry possesses few instruments, sometimes pressure gauges on the air supply to oil-fired furnaces, perhaps pressure and temperature gauges on the oil main, and sometimes a pyrometer hung up in the foreman's office to show to visitors.

Foundrymen say that the main reason for this lack of instrumentation is that the instruments offered are not satisfactory, but on the other hand the instrument makers do not seem to know much about foundries and have the impression that the non-ferrous foundry is not a useful market and that it is not worth developing instruments to suit it.

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The steel maker and even the steel founder is much better equipped in this respect, although his conditions are more difficult, and I suggest that the situation can be improved only by making the best possible use of such instruments as are available and complaining if they do not meet requirements.

Foundry pyrometry is by no means impracticable as regards reliability, cost (both prime cost and maintenance), and time taken to obtain a reading, but it is true that provision must be made for regular maintenance. Mr. French mentions on p. 313 the Chromel/Alumel type of thermocouple in a heat-resisting metal tube, and in my experience this is reasonably satisfactory for brass. For higher-temperature work with copper alloys and with phosphor-bronze in particular, the heat-resisting tube is attacked by the melt and does not last long, whilst replacements are rather expensive. The electro-graphite pyrometer tube gives a long life in copper alloys and cast iron provided that it is not damaged mechanically. It is, of course, much stronger than the silica tube employed in the steel foundry and can be used with a Chromel/Alumel couple up to about 1250° C., or with a platinum couple up to 1500° C. or above. The expense of replacement is not great, but care must be taken to avoid breakage; for example, by making the chargehand responsible for all temperature measurements. Response time is 25–40 sec.

With Chromel/Alumel couples in the graphite tube, contamination presents no problem provided that the couples are properly welded electrically, but with platinum couples, as Mr. French says, it is necessary to remake the joint now and again, and provision must be made for this in the design. The number of dips obtained before repair depends on the care and skill used in making the joint and on keeping the thermocouple clean. Some users get 30–40 dips and some only about 8.

As far as the indicating instrument is concerned, the ordinary portable instrument is less suitable for the foundry than the large robust quick-response indicator which is screwed to the wall and has a potentiometric circuit, so that plug-in points can be used beside each furnace. This arrangement is fairly expensive in first cost, but is quite reliable.

In some cases, as in the aluminium die foundry, it will be desirable to have a continuous indication of temperature so that the pyrometer tube must be in the bath all the time. So far as I know, there has never been an entirely satisfactory pyrometer tube for this job, as metal tubes dissolve in the aluminium, whilst refractory tubes are broken by the furnace operator or suffer from thermal shock. However, both types of tube are practicable if some care is taken.

Development work is in progress to produce a better tube both for aluminium alloys and for copper alloys, and at present it appears that a tube which will withstand continuous immersion in copper alloys for periods of, say,  $\frac{1}{2}$ –12 hr. will shortly be available.

With such a tube, it might be useful to link the pyrometer to a degassing tube so that the dual assembly could be immersed in the metal when it was molten and degassing could take place whilst the temperature came up to that required for pouring. One would then have a fully degassed melt at the right pouring temperature.

Dr. EMLEY and Mr. FISHER: We have one or two comments on the excellent and representative series of radiographs illustrating Mr. Fry's paper. Fig. 7 (Plate LVI) shows a typical example of layer-type microporosity, but we think Mr. Fry will agree that this type is not characteristic of the particular alloy, Z5Z, in which it occurred. With a full

zirconium content, Z5Z normally exhibits ribbon-type porosity running along rather than across the temperature gradient. If, however, the zirconium content is slightly deficient, layer-type porosity results. Both forms of porosity appear to be manifestations of mass-feeding, and it has been suggested by P. Spitaler that in the latter type the crystallites do not cohere sufficiently to form a spongy mass capable of developing the transverse "fractures" envisaged by Baker\* which become the sites of layer-type porosity. In this connection it is interesting to note that the slight reduction of zirconium content which causes the change-over from the ribbon to the layer type of porosity in Z5Z is accompanied by an increase in the amount of  $\beta$  phase—for zirconium increases the solid solubility of zinc in magnesium—and the development of dendritic structure in the grains, as well as an increase in grain-size. With a full zirconium content, the grains show pronounced rounded zirconium-rich cores in their centres, and it is known (see Dr. Emley's reply to discussion, p. 522) that these cores are very mobile in the earlier stages of solidification. It is therefore conceivable that some mobility is retained until an advanced stage, and that the slurry of crystallites repeatedly slips over the growing coherent solid skin of the solidifying casting. These "fault" sites may then become shells of relatively coarse grain with accompanying microporosity.

In Fig. 12 (Plate LVIII) the dense inclusions may, as Mr. Fry suggests, be attributable to reaction with moulding sand, but it is "mould reaction" rather than reaction with separate sand grains entrained in the metal stream that is involved, since the latter give rise to the very characteristic radiographic appearance shown in Fig. 2 (c) (Plate XLIII) of our paper.

We also have occasionally encountered core blows of the type illustrated by Mr. Fry (Fig. 15, Plate LVIII) and in the same pressure-tight alloy, ZRE1. It seems that the core acts in the same way as a blind riser applied to a skin-forming alloy.

Regarding Fig. 25 (Plate LXI), we wonder whether Mr. Fry could give further information on the origin of the flaky appearance mentioned. We ourselves have not found inclusions of the normal fluxes *per se* to show up distinctly in radiographs of magnesium alloys, although the structures with which any flux present would be likely to be associated, namely, oxide, porosity, or metallic particles, would themselves be visible. If some corrosion takes place owing to the presence of flux, either in microporous areas in the interior or at the casting surface before radiography, the corrosion product will be readily seen on the radiograph. Would Mr. Fry consider that Fig. 25 (Plate LXI) is an example of fluxy microporosity in which some internal corrosion has occurred? There appears to be a good deal of uncontaminated microporosity in the specimen.

Mr. Sharp calls attention to the need for precautions against flux inclusions in pressure die-casting magnesium and suggests fracturing a small bar cast with each batch of ingot as a check on ingot quality. The risk of flux inclusions will depend largely on the method of melting adopted. A few years ago we made several thousand cold-chamber pressure die-castings which were examined to Class I aircraft inspection requirements. The metal, ingot and scrap castings, was melted and refined with fluxes in the conventional manner, and transferred into a holding furnace fitted with a sulphur dome of the usual type. The metal was cooled below the liquidus and ladled in the pasty state into the pressure die-casting machine. No troubles at all with flux inclusions were encountered, but it was necessary to shot-blast the holding crucible, ladles, &c., in order to avoid iron scale in the castings.

\* W. A. Baker, *J. Inst. Metals*, 1945, **71**, 165.



## Discussion

# The Constitution of Tin-Indium Alloys in the Range 0-30 Per Cent. Indium

By J. C. BLADE and E. C. ELLWOOD

(*Journal*, this vol., p. 30)

Dr. C. W. GOULDING\* and Professor G. V. RAYNOR,\* M.A., D.Sc. (Member): In the course of investigations in the writers' laboratory relating to certain ternary alloys of tin, some experiments were carried out on the binary tin-indium system in an attempt to resolve discrepancies in the literature. The results of these experiments, though insufficient to establish the details of the tin-rich portion of the equilibrium diagram, are of interest in relation to the more complete work reported by Blade and Ellwood. In preliminary metallographic work, carried out on alloys annealed for 28 days at 50° C., it was observed that at 6.91 wt.-% indium, a small amount of  $\gamma$  persisted in the  $\delta$  matrix, and that at 24.00 wt.-% indium, traces of  $\beta$  in a  $\gamma$  matrix were present. These results are consistent with the work of Blade and Ellwood, but the very small amount of  $\delta$  we observed in a ( $\delta + \gamma$ ) alloy at 10.00 wt.-% indium is not consistent with the ( $\delta + \gamma$ )/ $\gamma$  phase boundary reported by these authors. To examine the possibility of the  $\gamma$  phase becoming unstable above about 80° C., as reported by Rhines, Urquhart, and Hoge,† an alloy containing 23 wt.-% indium was examined by X-rays, after annealing for 5 weeks at both 50° and 100° C. and quenching. No differences in the diffraction pattern, which agreed with that reported by Raynor and Lee,‡ were observed. Further, resistance/temperature experiments carried out with annealed and slowly cooled alloys containing 12, 15, 18, and 20 wt.-% indium revealed no indication of a transformation in the  $\gamma$  phase between -15° C. and the melting point. The resistance/temperature curves were smooth and continuous throughout. As an additional check, thermal analysis was carried out on an alloy with 15 wt.-% indium; an arrest was observed at 205° C., but no lower-temperature transformations were observed. This composition corresponds closely with the indium-rich limit of the  $\delta + \text{liquid} \rightleftharpoons \gamma$  peritectic line reported by Blade and Ellwood, and the arrest is in excellent agreement with their work. It is confirmed, therefore, that Rhines and his collaborators † were in error in confining the  $\gamma$  phase to low temperatures only.

In the resistance/temperature work, it was observed that the specimens, on slow heating (0.25°-0.5° C./min.), disintegrated at temperatures in the range 120°-200° C., the exact temperature depending on composition. Metallographic examination of the collected fragments revealed the presence of small amounts of chilled liquid, so that the temperature at which disintegration occurred may be taken as lying just within the ( $\gamma + \text{liquid}$ ) area in the phase diagram for the composition concerned. Thus, alloys containing 15.00, 20.97, and 21.50 wt.-% indium disintegrated at 182°, 145°, and 143° C., respectively; these results are again consistent with the  $\gamma$  solidus curve published by Blade and Ellwood. Limited metallographic work that was carried out on the  $\gamma$  solidus in general confirmed the present results. Thus, at 20.97 wt.-% indium, the alloy was homogeneous

$\gamma$  phase up to 140° C., but showed appreciable quantities of chilled liquid at 155° C.

In their paper, Blade and Ellwood suggest that variations of lattice spacing with composition in the tin-indium system are too small for X-ray lattice-spacing measurements to be used in locating phase boundaries in the solid state. The accuracy obtained in the work of Lee and Raynor,§ however, suggested to us that the method was capable of giving useful results. In this work, lattice spacings in the  $\delta$ -phase region were measured after annealing specimens for 2 weeks at 175° C. and quenching; although variation in the  $c$  spacing with

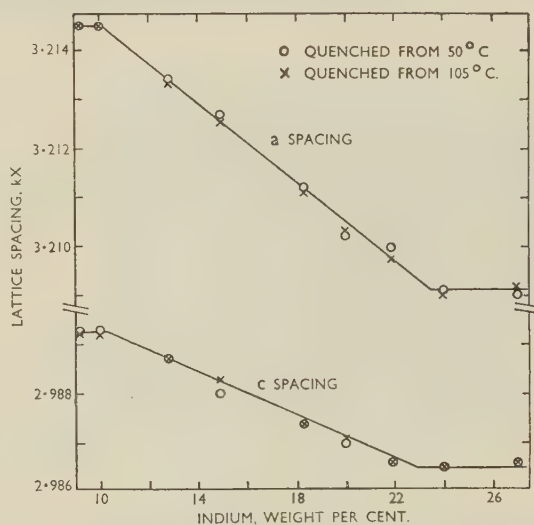


FIG. A.—Lattice Spacings of  $\gamma$ -Phase Tin-Indium Alloys.

composition was very slight, that of the  $a$  spacing was significant. Further work carried out by the present writers, using four homogeneous  $\delta$ -phase alloys, quenched from 50° C. after 5 weeks' annealing and from 105° C. after 10 weeks' annealing, gave lattice spacings differing insignificantly from those obtained by Lee and Raynor; for two-phase alloys, after similar annealing treatments, the following results were obtained:

Wt.-%	$a_{50^\circ}$	$a_{105^\circ}$	$c_{50^\circ}$	$c_{105^\circ}$
6.91	5.8151 kX	5.8152 kX	3.1750 kX	3.1750 kX
9.21	5.8152 kX	5.8151 kX	3.1749 kX	3.1750 kX

By combining these results with those of Lee and Raynor, the solid-solubility limit of indium in tin is derived as 5.7-5.8 wt.-% at both 50° and 105° C. This is in reasonable agreement with the work of Blade and Ellwood, and is con-

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† F. N. Rhines, W. M. Urquhart, and H. R. Hoge, *Trans. Amer. Soc. Metals*, 1947, 39, 694.

‡ G. V. Raynor and J. A. Lee, *Acta Met.*, 1954, 2, 616.

§ J. A. Lee and G. V. Raynor, *Proc. Phys. Soc.*, 1954, [B], 67, 737.

sistent with their suggestion that their published solubility curve is placed at compositions somewhat too rich in indium.

Lattice spacings within the  $\gamma$  phase field have also been determined. Here there is a significant variation in both the  $a$  and  $c$  spacings, as illustrated in Fig. A. Taken in conjunction with  $\gamma$ -phase lattice spacings in  $(\delta + \gamma)$  and  $(\gamma + \beta)$  alloys, which are also included in Fig. A, the tin-rich and indium-rich limits of the homogeneity range of  $\gamma$  may be derived as follows:

Tin-rich limit ( $50^\circ$  and  $105^\circ$  C.): 10.2-10.3 wt.-% In.

Indium-rich limit ( $50^\circ$  and  $105^\circ$  C.): 23.3-23.5 wt.-% In.

The indium-rich limit is in reasonable agreement with the work of Blade and Ellwood, but at a slightly lower indium content. The presence of chilled liquid in an alloy containing 22.98 wt.-% indium quenched from  $120^\circ$  C. supports the lower value. The tin-rich limit of the  $\gamma$  phase deduced from the lattice spacings is, however, significantly different from that reported by Blade and Ellwood. In view of the consistency of the X-ray results, it is difficult to account for this difference, particularly as the annealing times employed in the two researches are comparable. It is, however, equally difficult to escape the conclusion, on the basis of Fig. A, that the

homogeneity range of the  $\gamma$  phase is wider than that reported in the paper. In other respects, our experiments confirm the tin-rich portion of the equilibrium diagram as described by Blade and Ellwood.

THE AUTHORS (*in reply*): We wish to thank Dr. Goulding and Professor Raynor for their comments and are pleased to learn that their results confirm ours in practically all respects. We are at a loss to explain the discrepancy in the limit of the  $(\delta + \gamma)/\gamma$  boundary in their work and ours, particularly as the X-ray method we employed required positive identification of the pattern of the second phase before an alloy was recorded as being duplex. The small errors inherent in this procedure should have had the effect of narrowing, rather than broadening, the duplex field. Raynor and Lee\* have shown that structurally the transition from the  $\delta$  to  $\gamma$  lattice is quite a minor one. This being so, it may be more than usually sensitive to the presence of impurities, or even to mechanical and thermal treatment, so that the exact position of the boundary may be difficult to fix.

Apart from this discrepancy, however, Goulding and Raynor's confirmation of the general form of the diagram is of value in establishing that there are two solid solutions, both of which are stable from room temperature to the solidus.

\* G. V. Raynor and J. A. Lee, *Acta Met.*, 1954, **2**, 616.

#### CORRIGENDA

The following corrections should be made in the paper contributed by Mr. A. R. Martin to the Symposium on Metallurgical Aspects of the Control of Quality in Non-Ferrous Castings (*Journal*, this vol., p. 209):

p. 214, Column 2, 23 lines from bottom. For " $\bar{x} = \frac{Sx}{n} = -0.80$ " read " $\bar{x} = \frac{Sx}{n} = -0.08$ ".

Column 2, 18 lines from bottom. For " $t = \frac{0.80}{0.239} \times \sqrt{80}$ " read " $t = \frac{0.08}{0.239} \times \sqrt{80}$ ".

p. 221, Column 1, line 10. For " $S.E. = \frac{S.D.}{N} = \frac{0.04}{10} = 0.004 \text{ mm.}$ " read " $S.E. = \frac{S.D.}{\sqrt{N}} = \frac{0.04}{10} = 0.004 \text{ mm.}$ "

p. 226, Column 1, line 14. For " $\frac{a}{\text{residual}} = \frac{13.4}{1.217} = 11.0$  ( $p = 0.01 - 0.01$ )" read " $\frac{a}{\text{residual}} = \frac{13.4}{1.217} = 11.0$  ( $p = 0.01 - 0.001$ )".



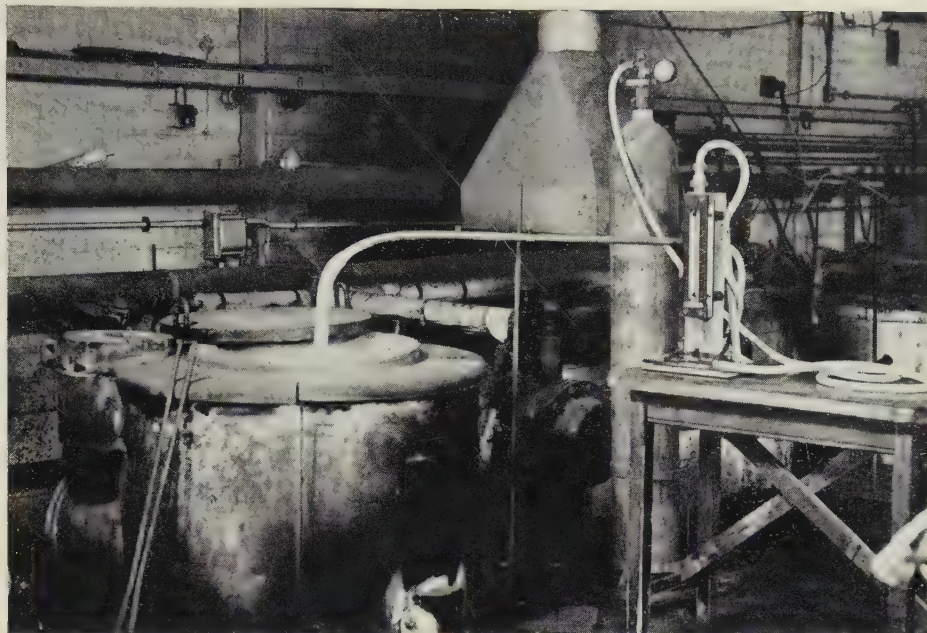


FIG. D3.—Arrangement for Control of Gas Content in Bale-Out Furnace. (Scheuer.)

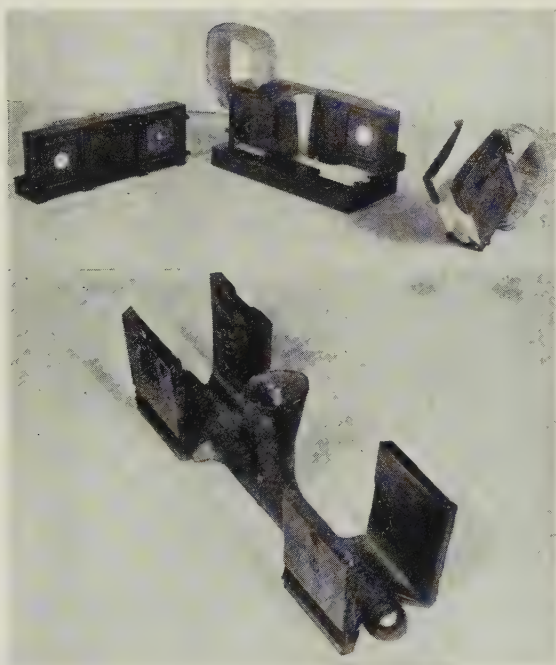


FIG. D4.—Hot-Spot Die for Examination of Surface Shrinkage. (Scheuer.)

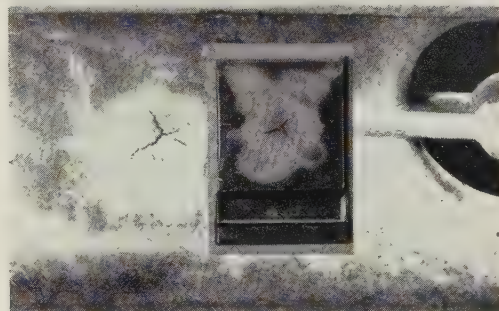


FIG. D5.—Hot-Spot Die-Casting and Production Casting in LM4 Alloy, Showing Identical Shrinkage Defects. (Scheuer.)

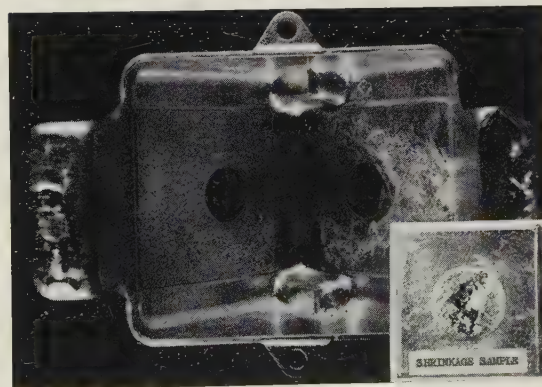
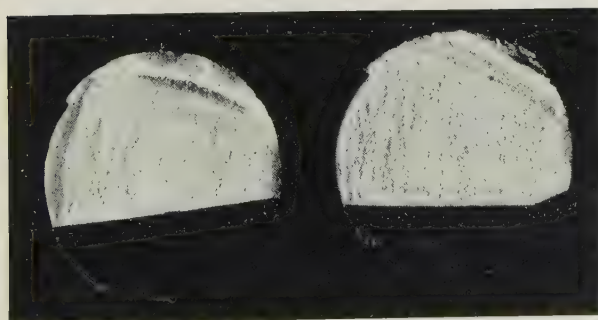


FIG. D6.—Hot-Spot Die-Casting and Production Casting in LM6 Alloy, Showing Identical Shrinkage Defects. (Scheuer.)

FIG. D7.—Fractured 1-in.-dia. Chill-Cast Bars of Binary Magnesium-Zirconium Alloy, Illustrating (a) a Satisfactory and (b) a Marginal Soluble Zirconium Content. (Emley's reply.)

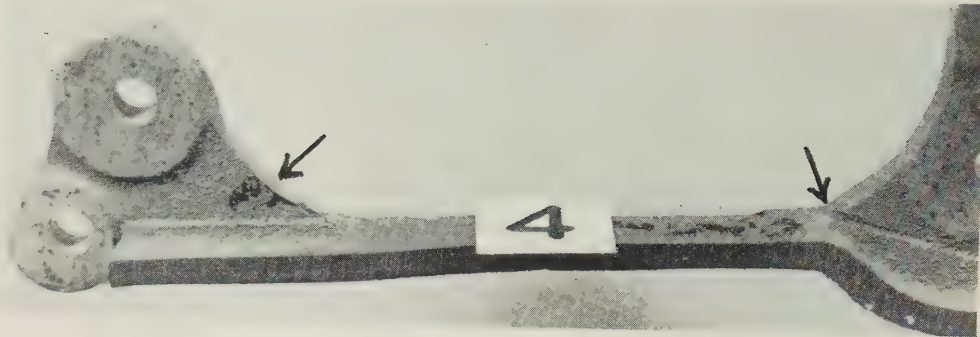


FIG. D12.—Class 1 Casting for Aircraft Construction (D.T.D. 298), Showing Cracks in Web Radii.

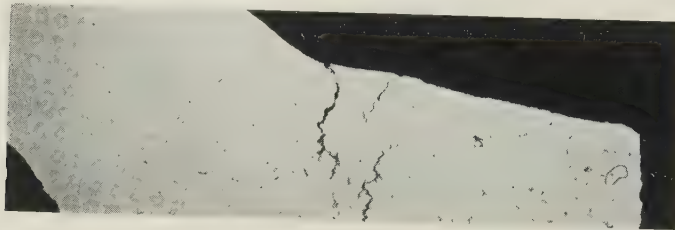


FIG. D13.—Microsection Through Crack from Casting Shown in Fig. D12.  
Unetched.  $\times 5$ .

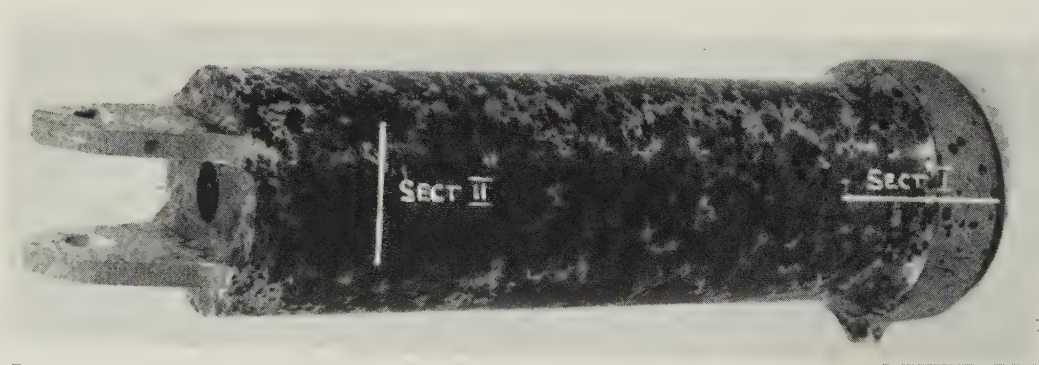


FIG. D14.—Class 1 (L53) Casting, Showing Extensive Staining After Chromic Acid Anodizing, due to Porosity.





FIG. D15.—Extent of Unsoundness Revealed in Section I Taken Through End of Casting Illustrated in Fig. D14. Unetched.  $\times 10$ .

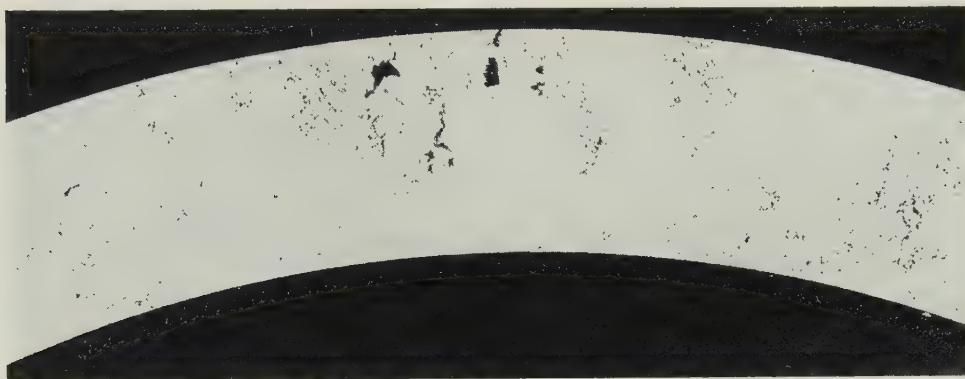


FIG. D16.—Extent of Unsoundness Revealed in Section II Taken Through Casting Illustrated in Fig. D14. Unetched.  $\times 10$ .

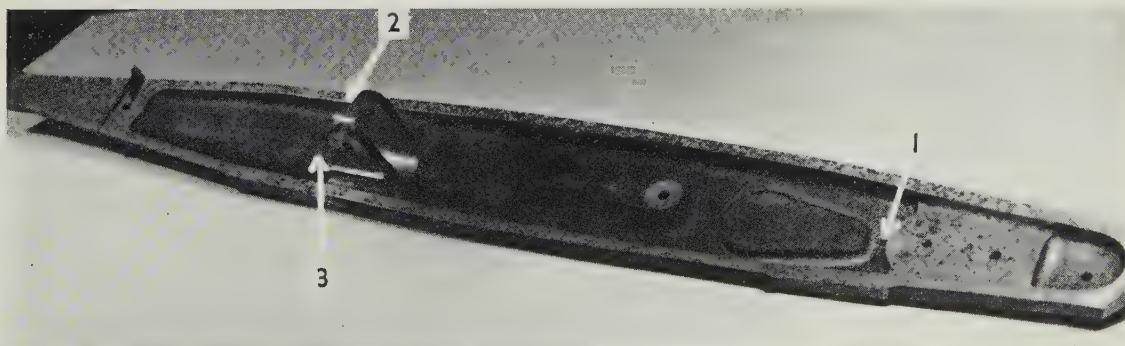


FIG. D17.—Class 3 Casting for Aircraft Construction (D.T.D. 298) as Anodized, Illustrating Defects Detected.

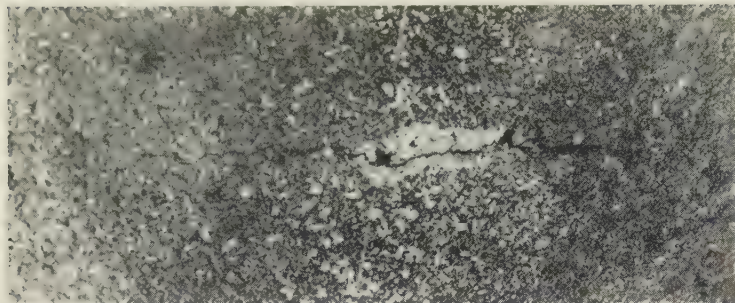


FIG. D18.—Crack Observed at the Surface (Position 1, Fig. D17).

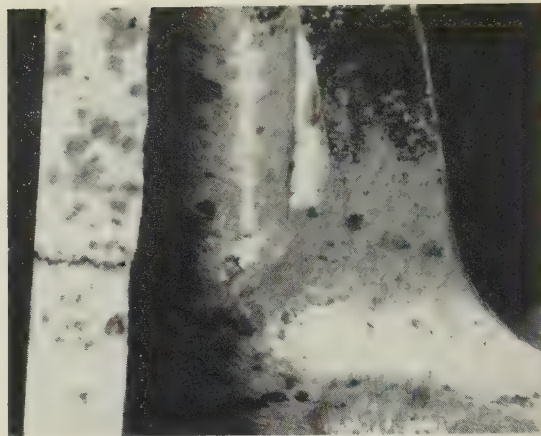


FIG. D19.—Crack Observed at the Surface (Position 2, Fig. D17).



FIG. D20.—Section Through Position 1 (Fig. D17). Unetched.  $\times 5$ .



FIG. D21.—Section Through Position 2 (Fig. D17). Unetched.  $\times 5$ .



FIG. D22.—Section Through Position 3 (Fig. D17). Unetched.  $\times 5$ .

(Evans.)



# Effect of Composition on the Stress-Corrosion of Aluminium Alloys \*

Miss M. K. B. DAY,† M.A., A.Inst P. (Member): The work described in my note was undertaken to provide a guide to the limit of the safe compositions which could be accepted in commercial practice if brittle segregates were to be avoided, and the number of melts examined was cut to a minimum. I regard it as forming a very slight part of a larger investigation on the properties of D.T.D. 687A-type alloys.

I feel that it is appropriate to present some results of work we have done on the effect of composition on the submicroscopic structure and general mode of precipitation in these alloys.‡ The structures have a bearing on the problem of stress-corrosion, as well as being complementary to the optical micrographs shown by Mr. Chadwick, Mr. Muir, and Mr. Grainger.

The electron micrographs on Plates LXXXII and LXXXIII are of anodic replicas taken from edge sections of 0.036-in. sheet, produced on a laboratory scale. Differences were first detected in the amount and distribution of the "precipitate", which appears white or very pale grey in the electron micrographs, in Al-5.9% Zn-2.9% Mg-1.4% Cu super-purity-base alloys containing 0.4% Mn (Figs. A-C) or 0.2% Cr (Figs. D-F). I am deliberately using the word "precipitate" somewhat loosely. It is impossible to determine from the electron micrographs whether an intermetallic phase has, in fact, been precipitated, or whether very small local concentrations of solute atoms are present in the aluminium solid solution. I do not propose to embark here on a discussion of the identity of the phases which may be precipitated. Mr. Varley, Mr. Sendorek, and I hope to publish shortly a paper covering the properties and structure of ternary Al-Zn-Mg alloys, and we plan to follow this with a detailed account of the structure of the more complex alloys.

In the Al-Zn-Mg-Cu-Mn alloy very little precipitate is apparent in the as-quenched state after 1 hr. at 465° C. (Fig. A), but during subsequent ageing at 135° C. preferential grain-boundary precipitation takes place, accompanied by some general precipitation within the grains (Figs. B and C). However, the scale of precipitation in the Al-Zn-Mg-Cu-Cr alloy is far heavier. Fig. D shows that an appreciable quantity is out of solution even in the as-quenched state, and this provides an explanation of the sensitivity in practice of the chromium-bearing alloys to rate of quenching, and of the fact that difficulty is sometimes experienced in achieving the required mechanical properties in thick plate and heavy forgings. General precipitation takes place in this alloy during ageing at 135° C., and the quantity and size of the precipitated particles shown in Figs. E and F are in striking contrast to the corresponding structures of the Al-Zn-Mg-Cu-Mn alloy. Attention should be drawn to the fact that the electron microscope has revealed the presence of denuded zones along some grain boundaries in both these artificially aged alloys, and, in fact, in the whole series of alloys examined. Although the denuded zones are more pronounced in the over-aged alloys (48 hr. or longer at 135° C.), they have been detected in alloys which had been aged only for 8 hr., as well as in those aged for 16 hr.

The structures of the basic Al-Zn-Mg alloy and its

quaternary variants were next examined and are illustrated by Figs. G-O (Plate B). Precipitation appears to take place in the Al-Zn-Mg and Al-Zn-Mg-Mn alloys in a manner similar to that observed in the Al-Zn-Mg-Cu-Mn alloy. It is only a little heavier in the Al-Mg-Zn-Cr alloy; although some coarse particles are apparent within the grains of this alloy, the grain-boundary structure with fine preferential precipitation is still akin to the manganese-bearing variants. On the other hand, precipitation is far more general and on a heavier scale in the Al-Zn-Mg-Cu alloy; an appreciable quantity is out of solution even in the as-quenched state, and Fig. O illustrates the structure after ageing for 48 hr.

As far as the mode of precipitation is concerned, it can be concluded that manganese appears to suppress the effect of copper, and that it is the combined effect of copper and chromium which accounts for the structure of the chromium-bearing quinary alloy.

Returning now to the question of the stress-corrosion of the alloys, during artificial ageing preferential submicroscopic grain-boundary precipitation is accompanied by the development of denuded grain-boundary zones, and this is in all probability associated with increased susceptibility to stress-corrosion. Then, as the grains themselves become over-aged, the difference in strength and potential between the grains and their boundary regions is reduced, the susceptibility to stress-corrosion decreases, and the minimum noted by Meikle§ on the "time-to-failure/duration-of-ageing" curve is passed. An alloy in which preferential grain-boundary precipitation predominates will exhibit these characteristics to a greater degree, and vice versa. Thus it would appear that the more general mode of precipitation in the chromium- and copper-bearing quinary alloy accounts for its superior properties, as much as does its elongated grain structure.

Dr. A. N. TURNER,|| B.Sc., A.R.S.M., A.I.M. (Member): There is a very good reason why the papers by Miss Day and by Mr. Chadwick, Mr. Muir, and Mr. Grainger should be grouped together for discussion. I should like to comment on this reason, for it is concerned with a most mysterious difference of practice between this country and North America. Miss Day explains the presence of chromium in commercial aluminium-zinc-magnesium alloys as being a function of mechanical properties. Now there are three probable mechanisms by which chromium may improve mechanical properties: by solution-hardening, the effect of which will be small owing to the restricted solubility of chromium in these alloys; by the inhibition of recrystallization, which can and does improve the tensile strength in the principal direction of working; and by preventing or retarding "decohesion" or intercrystalline weakness, which is also brought about by the presence of other elements, particularly copper.

A more commonly proposed reason for the addition of chromium, however, is to improve stress-corrosion resistance, a point brought out in the other paper under discussion. It is here that the difference in British and American practice

\* Joint discussion on the papers by R. Chadwick, N. D. SMITH, and H. B. Grainger (*J. Inst. Metals*, this vol., p. 161) and by (Miss) M. K. B. Day (p. 263).

† Research Laboratories of The British Aluminium Co., Ltd., Gerrards Cross, Bucks.

‡ M. K. B. Day and M. R. Smith, *Brit. J. Appl. Physics*, 1956, 7, 91.

§ G. Meikle, unpublished Ministry of Supply Report.

|| Head of Metallurgical Division, Aluminium Laboratories Limited, Banbury, Oxon.



becomes apparent. Almost all American specifications insist on a minimum chromium content of 0.18%; in this country, however, it is more normal either to use considerably less than this amount of chromium with a small addition of manganese, or to use a chromium-free alloy with about 0.5% manganese. As Miss Day has shown, there is a combined Mn + Cr content above which segregation of primary CrAl<sub>3</sub> occurs, but I would not agree that under practical conditions of semi-continuous casting the limit of primary separation is as she suggests. There is an incorrect assumption implicit in her statement that the rate of cooling under these conditions is faster than in her tests; in fact, the primary crystals form in the molten head by a process of selective deposition. However, whether the manganese-free alloy or the alloy containing Mn + Cr is used, the tendency is to maintain the Mn + Cr content close to the value at which primary, or "giant", chromium constituent will appear. We therefore have to ask ourselves what significance, if any, there is in the difference between American and British practice, and if, indeed, there is any necessity to maintain the additions of manganese and/or chromium at anywhere near the level at which casting difficulties begin.

Any information which will help us to resolve these problems is welcome, and for this reason the paper by Chadwick, Muir, and Grainger is timely. When other published information is studied, it is surprising to find that almost all of it refers to sheet materials. It is therefore unfortunate that the present paper also deals with sheet, for it should be emphasized that there are few worries industrially concerning the stress-corrosion behaviour of these alloys in sheet form or in the longitudinal direction in extrusions; it is in the transverse, and particularly in the short-transverse, direction in extrusions and forgings, that the trouble, which is very serious indeed, arises.

If significant improvements are to be made to the Al-Zn-Mg series of alloys—even, perhaps, if they are to survive at all as technically useful high-strength alloys—it is very important to determine the mechanism of stress-corrosion in them. Grain-size, grain shape, and the electrochemical effect of grain boundaries and precipitates situated there, are all mentioned as possibly being of significance.

Stress-corrosion in the alloys is a grain-boundary phenomenon and, therefore, must be at least in part electrochemical in nature. The first points to be decided are, therefore, whether the differences in potential which exist at grain boundaries are due to the presence of a precipitate, and, if so, whether this is less noble than the grain, in which case it would corrode, or whether it is more noble, in which case it would be the area of the grain adjacent to the precipitate which would corrode; whether the differences are due to the presence of a denuded zone of solid solution and, if so, its potential relative to the grain mass; or whether the differences are due to the presence of an equilibrium segregation of zinc and/or magnesium at the boundaries.

Then the influence of the purely mechanical aspect of the grain boundaries must be considered. There is evidence to suggest that the amount of corrosion damage which takes place in these alloys during a stress-corrosion failure is small, but that once cracking has begun it proceeds very rapidly along a grain-boundary weakness, although the continual presence of a corrosive medium appears to be necessary. The weakness could be a precipitate (brittle or soft), a denuded zone (soft), or a zone enriched through equilibrium segregation (possibly hard). In any case, the presence of stress-raisers such as oxide, porosity, or insoluble constituents would be expected to increase the ease of cracking.

If the mechanism of cracking is such as that described above—that is, electrochemical in origin but mechanical in continuation—then it should be possible to influence it considerably by variations in composition and heat-treat-

ment. That this is so has been shown in the paper by Chadwick, Muir, and Grainger (effect of copper) and by Meikle\* (effect of precipitation-treatment). One must ask here, however, what is the mechanism of the effect of chromium in apparently improving the stress-corrosion resistance considerably. If it is by refining the grain-size and altering its shape, then there is a distinct possibility of losing in the transverse direction what is gained in the longitudinal. In the short-transverse direction, the stress-corrosion properties appear to be governed very largely by factors other than minor variations in composition; what these factors are is uncertain, but they may be associated with imperfections in the material originating in the casting, although variations in structure which are themselves a function of ingot quality/fabricating technique/composition interactions may also play a part.

If there is more to the influence of chromium than an alteration in grain shape, it may be connected with a direct effect on the potential characteristics of whatever substance exists at the grain boundaries; it may affect the diffusion of zinc and magnesium to the boundaries or prevent them from concentrating there, or it may act as a nucleus for the precipitation of zinc and magnesium in regions other than grain boundaries, thus leading to a more balanced potential relationship. There is evidence, both micrographic and indirect as a result of the quench-sensitivity of chromium-containing alloys, that chromium does lead to an easier and more general precipitation. Whether this has a significant effect on stress-corrosion or not is less certain. It would, however, be expected by analogy with the work of Meikle,\* which shows that over-ageing leads to an improvement in stress-corrosion resistance.

To sum up, then, basic work on the stress-corrosion mechanism is of extreme importance to these alloys. This work should include a study of the grain-boundary condition, not only from the point of view of the presence of zones of different potential, but also from the point of view of the existence of paths of easy fracture—a problem which is of importance quite apart from stress-corrosion. It would be a misfortune if the very attractive properties offered by the alloys could not be fully utilized because of misgivings about stress-corrosion and, I would add, crack propagation and fatigue characteristics, all of which, I believe, may have a common basic cause.

Dr. F. A. CHAMPION, B.Sc., A.R.C.S., F.I.M. (Member): The paper by Mr. Chadwick, Mr. Muir, and Mr. Grainger reports some most interesting results on a topical subject, but I wonder whether the authors regard the stress-corrosion results as anything more than exploratory, in view of the method of production of the metal. Laboratory rolling mills tend to be maids-of-all-work, and my experience has been that metal finished on such mills is apt to be unreliable for corrosion tests intended to represent normal production. We use a technique for stress-corrosion tests somewhat similar to that described by the authors: the jigs are accommodated in a room, rather than a cabinet, of controlled atmosphere, but they are carried in close proximity on metal frames, and we find a much less elaborate provision for shock absorption to be adequate.

Can the authors explain why they chose 1.25% copper for further tests, when their earlier results suggest that this gave a higher stress-corrosion susceptibility than 0.35% copper if the beneficial effect of iron is taken into account (e.g. WZ7 and WZ8 of Table I (p. 163) and Table IV (p. 166)? To aid such interpretation of the results, can the authors add the missing iron contents to Table I? I would also suggest that the increase in stress-corrosion life which the authors have attributed to grain refinement is more likely to be due to variations in iron content. In the illustration of this given

\* G. Meikle, unpublished Ministry of Supply report.



in Table A, drawn from the authors' results, the lives quoted are for the alloys aged at room temperature and stressed at 50% of the proof stress, since it is difficult to find a complete series for the artificially aged specimens.

On p. 166, the authors state that the maximum safe level of stressing can be raised to approximately 20 tons/in.<sup>2</sup>; how would this figure be affected by changes in the initial metal thickness or the corrosion conditions as compared with those used in the authors' tests? On p. 167, they refer to the lack

TABLE A.—Effect of Iron Content on Life of Al-Zn-Mg Alloys.

Mark	Life, hr.	Grain-Size, approx. mm.	Iron Content, %
WZ1 . . .	0.05	0.25	0.01
WZ6 . . .	1.8	0.05	0.14
WZ4 . . .	0.1	0.05	0.015
WZ9 . . .	1.0	0.05	0.12

of correlation between the results given in Table V for salt spray and salt-peroxide solution, respectively; from my experience of these media I would regard the former as giving the more reliable evidence of practical significance. I should, therefore, be interested to know whether the grain-centre attack shown in Fig. 19 (Plate XXX) was observed without, as well as with, hydrogen peroxide. The authors argue (p. 169) that the grain centres are anodic to the grain boundaries, but if this is so, why are stress-corrosion fractures invariably intercrystalline?

Mr. CHRISTOPHER SMITH,\* F.I.M. (Member): In considering the detail of stress-corrosion testing, or for that matter any kind of corrosion testing, it is essential to take into account not only the material, but also the conditions under which it is to be treated in service.

Most of the failures which have given the Al-Zn-Mg alloys their bad reputation have occurred under conditions where considerable internal stresses existed, and almost exclusively in cases where the stresses were in a direction transverse to the grain direction. I learn with regret that Mr. Chadwick and his colleagues do not propose to continue their work on these alloys, because the conclusions so far arrived at bear no relationship whatever to anything but sheet material, in which there have been no service failures at all.

A great number of the early failures arose from internal stresses induced in components by quenching stresses at the heat-treatment stage, which were intensified by subsequent machining. In some cases components actually fractured spontaneously within minutes of being machined, and this fact gives some indication of the extremely high stresses which existed in components actually built into aeroplanes. Today, it is the universal practice to quench in boiling water such components as cannot be subjected to a controlled stretching operation after heat-treatment. In this way the induced stresses are reduced to a safe level. The second method of reducing internal stress, that of controlled stretching after heat-treatment, is now practised on all components which have to be machined. However, in many such cases components may later be put into a dangerous condition of internal stress, as, for example, where thin sections are machined from the centres of large extrusions, and these thin sections have rows of holes drilled in them through which rivets are subsequently driven, sometimes without any apparent attempt being made to check the exuberance of the riveter. Internal stresses up to 90% of the ultimate stress of the material may thus arise.

All these facts are directly relevant to the failures which have given these alloys a bad reputation and must be considered in relation to any programme of stress-corrosion testing if it is to give an answer which can be applied in practice.

It would seem therefore, that these materials should be tested with the grain direction normal to the applied stress, in which case the authors' observation on the effect of chromium on grain shape probably has no significance at all. In this connection Miss Day's work is much to the point. I congratulate her on the excellence of her photographs and would express the opinion that along the lines she is following may well come the answer to this difficult problem.

The older alloys, which, it is claimed, are not susceptible to stress-corrosion failure because of their wider plastic ranges and much lower elastic limits, are incapable of building up the high levels of internal stresses which arise in the Al-Zn-Mg alloys, because if they are maltreated they yield, and so the level of internal stress is inevitably low, very much lower than in the ultra-strong materials now under discussion. Is not this an important factor which must also be borne in mind when initiating corrosion-testing programmes?

Mr. A. CIBULA,† M.A., A.I.M. (Member): The paper by Mr. Chadwick, Mr. Muir, and Mr. Grainger forms an interesting complement to another recently published by Martin‡ on the influence of various ageing treatments. It is possible to determine, from the results of the two investigations, the alloys in which susceptibility to intergranular failure is likely to be encountered in sheet material under tensile stress, with or without corrosion. The present authors should be congratulated on their experimental techniques, the high standard of which is demonstrated particularly by the consistency of the stress-corrosion lives.

I should differ from the authors on two points only. The first concerns their use of the term "safe level of stress". Although I do not wish to exaggerate the precision which they attach to this term, it may be misleading. Such a limit appears to exist when the applied stress is plotted against the logarithm of the life, but it is in fact difficult to extrapolate curves of the shape obtained. Some extrapolation is indeed essential if the duration of the test is limited to 100 days, for the degree to which failure is accelerated in the salt-spray test, in comparison with service conditions, may easily be overestimated; Miss Whitaker§ has studied the influence of the corrosive environment in some work on similar alloys at the British Non-Ferrous Metals Research Association and has found that the stresses required for equal stress-corrosion lives in specimens sprayed with distilled water or salt solution, or simply exposed to moist air, differ only by about 10% of the proof stress. Miss Whitaker has confirmed a suggestion by several German workers|| that if the logarithm of the reciprocal of the stress-corrosion life (i.e. the stress-corrosion "rate") is plotted against the logarithm of the stress, a straight-line relationship is obtained. This line apparently cannot be extrapolated to an infinite life at any finite stress, and the term "safe level of stress" should be used with caution, therefore.

My second point of difference relates to the reason which the authors put forward for the beneficial influence of chromium on stress-corrosion resistance, i.e. its effect on grain shape. The difference between the paths of fracture shown in Figs. 20 and 21 (Plate XXX) is admittedly significant; it hardly seems great enough, however, to account for the large effect on stress-corrosion susceptibility, as the authors' results indicate that the life is not greatly affected

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† Head of Casting Section, British Non-Ferrous Metals Research Association, London.

‡ A. J. Martin, *Metal Ind.*, 1956, **89**, 511, 531.

§ M. E. Whitaker, British Non-Ferrous Metals Research Association, unpublished work, 1956.

|| e.g. O. Lissner, *Z. Metallkunde*, 1943, **35**, 79; 1948, **39**, 66.

by the time taken for the fracture to wend its way across the specimen. Once the fracture has started, complete failure rapidly ensues, and the life depends rather on the time taken to initiate the fracture. The fact that chromium prevents selective grain-boundary corrosion in certain of the alloys studied supports the suggestion made by Dix\* that this element affects the microstructure at the grain boundary and the uniformity of precipitation, and that these effects are responsible for the improvement in stress-corrosion resistance.

I should be grateful for any information which the authors may have about the composition of the precipitates formed in alloys aged at 125° C. They appear to assume that the precipitates are the same as the equilibrium precipitates at 200° C., but there is evidence that the composition varies with ageing temperature.

The Al-Zn-Mg alloys are particularly interesting because not only are they sometimes susceptible to stress-corrosion, but they may also be strongly affected by notches in ordinary tensile tests. Although the latter property may be partly due to the high proof stress of the alloy, it is not entirely so, because the mode of fracture, too, is affected, becoming intercrystalline in notched specimens. This type of notch-sensitivity suggests that there is a marked difference in the mechanical properties of the grain boundary and the interior of the grains, and that this leads to premature rupture near the grain boundary when the normal stress is high, as in triaxial stress systems at the roots of notches.

It seems possible that the factors causing notch brittleness may also participate in true stress-corrosion failure, for both types of fracture are largely intercrystalline. Whether or not this suggestion is correct, the selective attack of the grain boundaries during stress-corrosion leads eventually to the formation of a notch having the same deleterious effects, presumably, as one machined into the specimen. The local stress initially increases as the notch deepens, and the final rapid stage of failure described by the authors may therefore be the result of notch brittleness, rather than stress-corrosion, i.e. it is largely a premature mechanical failure. The life of the specimen would thus be greatly shortened, but it would nevertheless still be determined by stress-corrosion properties controlling the formation of the notch.

In wrought alloys longitudinal stringers of intermetallic constituents may be present, which may themselves have considerable notch effects in short-transverse specimens. It seems likely that the associated stress concentrations hasten the failure by stress-corrosion of such specimens, as the effective stresses, even at the beginning of the test, may be locally considerably higher than the applied mean stress. The stress-concentration factor may apparently be as high as 2 or 3, and the very great susceptibility to stress-corrosion in the short-transverse direction of large wrought products may thus be explicable, bearing in mind the sharp reduction in life which occurs when the stress is increased beyond a certain level.

It should also be remembered that while an elongated grain structure necessarily prolongs the path of intergranular fracture in longitudinal specimens, it has, if anything, the opposite effect on the fracture in transverse specimens, and no beneficial effects may therefore be expected on the properties in this direction.

For these reasons one would expect to find considerable differences in stress-corrosion properties in the longitudinal and transverse directions, and the conclusions drawn by the authors and by other workers about the stress-corrosion properties of sheet materials must be applied with caution to wrought materials stressed transversely. Evidence of the influence of chromium, for example, on transverse stress-corrosion resistance is exceedingly scanty, and the little that exists is conflicting. On the other hand, treatments which affect the size of stringers would probably have a large

influence on transverse stress-corrosion properties, though having little effect on longitudinal properties; for this reason one would expect a large scatter in the short-transverse properties of wrought products of nominally the same composition and state of heat-treatment, but differing in metallurgical history.

Mr. G. MEIKLE,† B.Sc., F.I.M. (Member): The paper by Mr. Chadwick, Mr. Muir, and Mr. Grainger forms a most useful contribution to our knowledge of the stress-corrosion properties of the Al-Zn-Mg alloys, especially with regard to the effect of chemical composition. At the Royal Aircraft Establishment, Farnborough, we have studied to a very considerable extent the atmospheric stress-corrosion of these alloys and the reference on p. 164 of the paper to my advocating a higher ageing temperature is based on this work. It has been found that the stress-corrosion susceptibility of these alloys is dependent, not only on temperature of ageing, but also on the time at the ageing temperature. Fig. P

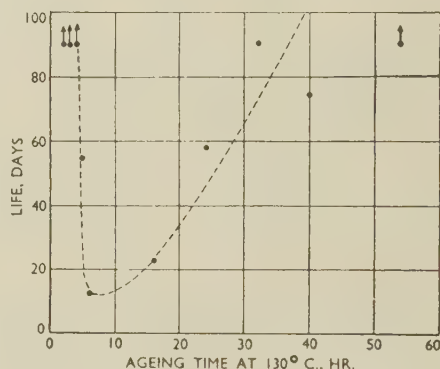


FIG. P.—Stress-Corrosion Life of Aluminium-Zinc-Magnesium Alloy (R.R. 77) Solution-Treated at 465° C. (870° F.) and Aged at 130° C. (266° F.). Arrows indicate unbroken specimens.

illustrates some of the results obtained on specimens of Al-Zn-Mg alloy (R.R. 77: Zn 5.39, Mg 2.63, Cu 0.40, Mn 0.47, Si 0.26, Fe 0.35%, Cr nil) tested, in the form of specimens  $6 \times \frac{3}{4} \times \frac{1}{4}$  in., by bending under four-point loading with 90% of the 0.1% proof stress applied. It will be noted that the under-aged specimens give good results, but subsequent tests after further ageing at room temperature for 15 months have indicated that the instability of the under-aged alloy has increased the susceptibility to stress-corrosion. To illustrate the effect of time and temperature, the following figures show the minimum ageing time at different temperatures which gave unbroken test-pieces after 90 days under 90% of the 0.1% proof stress, the material being a large D.T.D. 683 (Zn 6.12, Mg 2.96, Cu 1.16, Mn 0.35, Si 0.29, Fe 0.38, Cr 0.17%) extrusion tested in the long transverse direction:

Temp., °C.	Time, hr.	0.1% Proof Stress, tons/in. <sup>2</sup>
100	168	31.7
120	48	30.9
130	20	31.0
150	4	29.3

It will be noted that the treatment at 150° C. for 4 hr. gave a lower proof stress than the other temperatures, but 6 hr. at 150° C. gave a proof stress of 31.2 tons/in.<sup>2</sup>, with immunity from stress-corrosion. We have also found that the temperature of solution-treatment has an appreciable effect on the stress-corrosion susceptibility. Fig. Q shows the effect of solution-treatment temperatures of 465° and 435° C. on

\* E. H. Dix, *Trans. Amer. Soc. Metals*, 1950, **42**, 1057.

† Royal Aircraft Establishment, Farnborough, Hants.



specimens of the same D.T.D. 683 extrusion aged at 120° C. A further series of tests was made on this material solution-treated at 525°, 480°, 465°, and 435° C., ageing in each case being carried out at 130° C. The results are shown in Fig. R, from which it will be seen that lower solution temperature favours better stress-corrosion resistance.

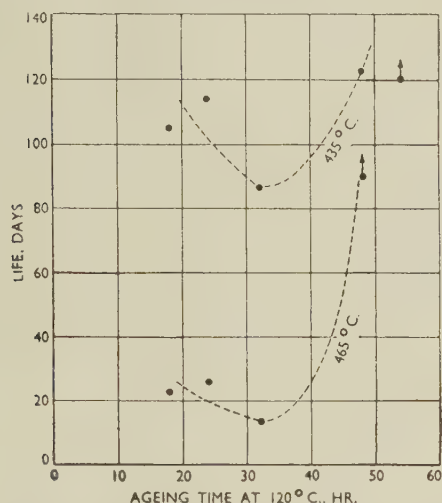


Fig. Q.—Stress-Corrosion Life of Aluminium-Zinc-Magnesium Alloy (D.T.D. 683) Solution-Treated at 465° C. (870° F.) and 435° C. (815° F.) and Aged at 120° C. (250° F.) Stressed to 90% of 0.1% proof stress. Arrows indicate unbroken specimens.

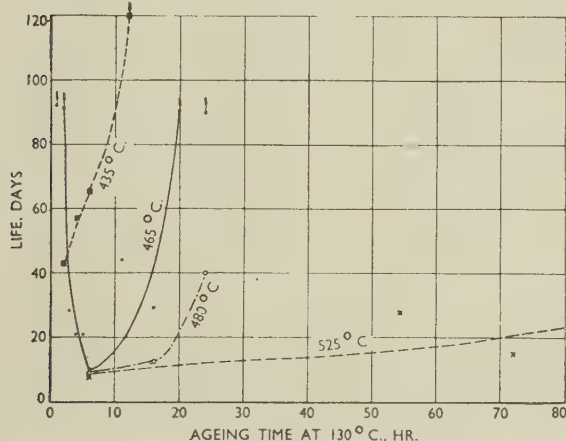
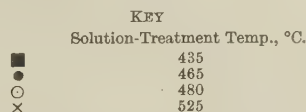


Fig. R.—Effect of Solution-Treatment Temperature on Susceptibility to Stress-Corrosion of Aluminium-Zinc-Magnesium Alloy (D.T.D. 683). Stressed to 90% of 0.1% proof stress. Arrows indicate unbroken specimens.



In the paper under discussion, Table IV (p. 166) gives some very interesting information, but I am a little disturbed at the number of specimens which failed during loading. Since these materials apparently underwent successful tensile tests (Table III, p. 165) it is difficult to understand why they should have failed before reaching the proof stress unless the stressing apparatus was giving non-axial loading.

A most interesting feature of these results is the improvement in susceptibility to stress-corrosion exhibited by commercial-purity material. We can confirm this tendency from our own work at the R.A.E. In a particular development, we made a forged block from high-purity materials which gave very good results. We then asked one of the aluminium alloy manufacturers to make up a large forged block of the same composition and the results, as judged by tests on material aged at 120° C., were better with the commercial than with the high-purity material. Similar results have been communicated to us privately by Professor W. R. D. Jones, with reference to tests on sheet material.

The statement in col. 1 of p. 166 that "in many of the alloys 2400 hours' testing is adequate to provide an approximate value of the maximum safe level of stressing for a particular alloy" should be treated with caution. Experience at the R.A.E. over many years of stress-corrosion testing has convinced us that it is unwise to attempt to translate stress-corrosion results of the type reported in the paper into terms of practical stressing of structures. We prefer to regard such tests as merely "sorting tests", either to separate different compositions or to indicate the relative utility of different heat-treatments. Although, like the authors, we may report actual numerical values, we mentally divide the results into the broad categories of "good", "bad", or "indifferent".

Mr. A. SENDOREK,\* Dipl.Met.Ing. (Member): I should like to make some comments on the level of tensile properties for the Al-Zn-Mg alloys, quoted by Mr. Chadwick, Mr. Muir, and Mr. Grainger.

I have been investigating the structure and mechanical properties of the high-purity Al-Zn-Mg alloys and the effects of alloying additions on their structure, strength, and ductility in the form of sheets 0.036 and 0.064 in. thick.

On the basis of the results obtained for alloys in the naturally and artificially aged conditions, I consider that the low tensile properties given in Table II (p. 164) for naturally aged alloys containing more than 7.4% Mg + Zn can with greater probability be attributed to the presence of intercrystalline cracks, than to the intercrystalline brittleness normally developed during the age-hardening process in these alloys. I feel almost certain that such cracks must have occurred in a good proportion of the tensile specimens during the period of natural ageing, probably as a result of quenching stresses induced by the slightly uneven quenching of the tensile samples in their final shape.

I have obtained similar low properties due to this kind of crack for alloys of comparable compositions and conditions on some tensile specimens 0.036 in. thick which were punched from the sheet material before solution-treatment.

The tensile samples of 0.064-in.-thick sheet which I quenched in the strip form and milled soon after quenching, did not exhibit such defects, and all gave tensile figures consistent with their compositions. In the material naturally aged for 1 month, a very marked deterioration of ductility was shown by samples with just over 9% Mg + Zn at a proof stress of more than 15 tons/in.<sup>2</sup> and a tensile strength of about 24 tons/in.<sup>2</sup>. In most of the alloys investigated, the proportion of magnesium to zinc was higher than in the alloys studied by Mr. Chadwick and his colleagues. I did not detect any stress cracks in samples of the ternary alloys aged at 135° C. for 16 hr. with only a short interval between quenching and artificial ageing.

The tensile samples of alloys containing iron, silicon, copper, manganese, or chromium became immune from cracking unless an external stress was applied, in both the naturally and artificially aged conditions. Thus, the level of properties stated by the authors for the artificially aged ternary alloys and the more complex alloys is comparable

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with the level which I obtained for similar alloy compositions after both types of ageing.

Dr. W. M. DOYLE,\* M.Eng., F.I.M. (Member): For many years we have been carrying out an extensive research programme into the stress-corrosion characteristics of ternary and more complex alloys in the system investigated by Mr. Chadwick and his colleagues. One of the original objectives of this work was to try to improve the stress-cracking susceptibility, which sometimes causes failure in commercial forgings and extrusions, especially when they are stressed in the short-transverse direction. As in the case of the present work, our specimens were made in the form of laboratory-rolled sheet and the actual stress-corrosion testing was carried out at the Metallurgy Department of the Royal Aircraft Establishment, Farnborough.

The results of our work in general agree with the findings of the present authors, but unfortunately the stress-corrosion testing of these alloys in the form of sheet does not bear very much relation to the metallurgical factors, such as grain flow and grain-size, which exist in the short-transverse

in tests taken from a series of forged blocks of similar composition and forged in the same manner. It is possible to choose results indicating that chromium has a beneficial effect on the stress-corrosion performance and a second selection of test results will indicate the converse.

Table B shows some typical results obtained on commercial alloys in the Al-Zn-Mg series. The tests include alloys containing manganese, such as R.R. 77; the alloy designated D.T.D. 683, which contains a relatively large amount of manganese in addition to a normal amount of chromium; a chromium containing 75S-type alloy; and finally, three similar melts in the new American alloy 7079, which is merely a re-issue of the alloy developed in Germany during the War and known as Hydronalium 43. All the tests were carried out in triplicate, and the life in days is shown in the last column of the table. It can be seen from these results that, in the case of forgings, the addition of chromium is not necessarily the answer to the stress-corrosion problem.

I should also like to take this opportunity of pointing out that the internal stress due to the quenching of large forgings is a very important factor affecting the possible failure of

TABLE B.—*Summary of Atmospheric Stress-Cracking Tests on Forged Blocks.*

Specimens taken in short-transverse direction.

Alloy	No.	Composition, %					Solution-Treatment		Temp. of Quench Water, °C.	Ageing Treatment		Tensile Properties			Life, days
		Zn	Mg	Cu	Mn	Cr	hr.	°C.		hr.	°C.	0.1% P.S., tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	Elong., %	
R.R. 77	1	5.46	2.68	0.41	0.53	...	4	465	85	12	135	28.9	32.6	1.5	105U, 118, 130
	2	5.33	2.58	0.38	0.50	...	4	465	85	12	135	29.5	33.7	4.3	42, 43, 61
	3	5.52	2.84	0.43	0.52	...	6	460	85	12	135	28.7	31.9	2	39, 52, 52
	4	5.46	2.66	0.39	0.51	...	4	460	85	12	135	29.8	34.0	2	7, 31
	5	5.54	2.79	0.42	0.53	...	4	465	85	12	135	29.2	32.4	2	36, 95
	6	...	...	...	...	...	4	460	Boiling water	12	135	29.8	33.6	2	88, 118
D.T.D. 683	7	5.64	2.65	1.4	0.76	0.14	4	465	85	12	135	25.9	30.9	3	38, 64, 72
75S	8	5.62	2.63	0.92	0.02	0.16	6	460	20	24	120	27.0	34.0	5	31, 33, 68
7079	9	4.52	3.2	0.59	0.04	0.16	4	465	20	24	120	27.9	33.1	5	32, 33, 42
	10	4.56	3.14	0.58	0.01	0.20	6	443	20	48	115	25.7	31.5	3	25, 76, 83
	11	4.52	3.2	0.59	0.04	0.16	4	444	20	48	115	29.2	33.7	4.5	11, 18, 20

U = unbroken.

direction of forgings and extrusions. In any case, there is no commercial specification covering the use of unclad sheet, and the alloys in sheet form are always used as-clad with an aluminium alloy containing 1% zinc. The cladding is very effective in preventing failure by stress-corrosion, and therefore there is no practical application of any stress-corrosion tests carried out on these alloys in the form of unclad laboratory-rolled sheet.

In addition to the work on sheet described above, we have undertaken an extensive series of tests under atmospheric stress-corrosion, in bending, on sections cut from the short-transverse direction of large forged blocks, with a cross-section of 15 × 7 in., using a test rig very similar to that described by Mr. Meikle. The benefits that can be derived from the addition of chromium to the Al-Zn-Mg type of alloy in the form of sheet have not been confirmed on this alternative source of test material. The testing has been carried out under stresses equal to 90% of the measured 0.1% proof stress of the material tested in the same direction and, whilst the results of tests taken from one source of material are consistent, a considerable scatter of results may occur

components in service. In this connection, any of these alloys which contain chromium must be quenched in relatively cold water in order to maintain the specification properties and, hence, the danger of internal stress is much more severe in this type of alloy. On the other hand, the commercial alloys containing manganese and no chromium, such as R.R. 77, permit the quenching to be carried out in boiling water, which minimizes the level of internal stress and, at the same time, the full specified tensile properties can be obtained.

We are currently carrying out investigations in connection with the quenching of, and additions of other elements to, these alloys which indicate that we may be able materially to reduce the difficulties associated with the stress-cracking tendency of forged components.

Dr. H. K. FARMERY,† M.A. (Member): Mr. Chadwick, Mr. Muir, and Mr. Grainger are to be congratulated on presenting a large amount of data in such a concise form without undue confusion. The title of their paper is slightly misleading, since only sheet material was used and this in

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† Fulmer Research Institute, Stoke Poges, Bucks.



effect meant that tests could be carried out only in the longitudinal and long-transverse directions. Directionality of structure is, in this case, a decided advantage, whereas with large extrusions or forgings stressed in the short-transverse direction, the opposite may be true.

Although agreeing that the method of stressing is elegant and apparently quite efficient, I think it would have been useful to carry out some comparative tests with specimens stressed in bending, since sheet material will inevitably experience bending stresses in practice. It might be expected that in certain circumstances, directional material would fail more rapidly in bending than under direct tension.

The surface condition of any material can influence its subsequent corrosion-resistance, and this is particularly true of aluminium and its alloys; since the authors took great pains to ensure a reproducible system of stressing, would it not have been equally desirable to start with a standard surface finish on the various alloys tested? During the solution-treatment of magnesium-containing aluminium alloys, a greyish oxide film is produced which contains magnesia both on the outer surface and within the film, the proportions of which vary with the original magnesium content. This magnesia produces initially an alkaline electrolyte when the material is wetted, and so delays the onset of localized corrosion; it would seem more satisfactory therefore to start corrosion tests with an etched surface. Since the Al-Zn-Mg alloys appear to be very sensitive to intergranular failure even in moist or slightly contaminated atmospheres, it would be interesting to know, with reference to Table II (p. 164), whether the specimens aged for 3 weeks at room temperature were exposed to the laboratory atmosphere during this time or stored in a desiccator.

In Table III, (p. 165) it is stated that exfoliation is produced in the salt-peroxide test on Series III material aged at room temperature, but not when aged at 125° C.; can the authors explain this important difference and also give some indication of the paths which such foliation follows? The interesting feature is that it can apparently occur on equiaxed material, such as XWE (Fig. 20, Plate XXX). Exfoliation appears to be connected with the combined presence of copper with manganese and/or chromium. Does this in effect mean, as with H15, that stress-corrosion and layer-corrosion are competitors, one evil often being reduced only at the expense of the other?

The curves shown in Figs. 2-5 (p. 167) relating applied stress to time to fracture are very interesting in as far as no one curve crosses another. This fact can be of comfort to any investigator carrying out comparative tests on similar materials, who has not the facilities or time to test each alloy over a wide range of stresses. Whilst testing at a high stress level will not give any indication of a possible "threshold stress", it will, apparently, from these results place alloys in their correct order of susceptibility over a considerable stress range.

In Table V (p. 168) several discrepancies are shown between specimens tested in salt spray and those totally immersed in salt-peroxide solution. Do the authors think that these are due to the method of testing or to the different behaviour in the two electrolytes; if the latter, do they still consider the salt-peroxide solution a satisfactory accelerated-testing medium?

The effect of copper in reducing the tendency to stress-corrosion cracking appears to be due to an equalization of potentials through more uniform precipitation, rather than, as ascribed in the paper, to making the grain interiors more anodic; the addition of copper to aluminium raises the potential rather than lowers it. With reference to the type of attack shown in Fig. 19 (Plate XXX), we have noticed

a similar effect in aluminium-copper-cadmium alloys exposed to both marine and industrial atmospheres. In the under-aged condition, attack is mainly intercrystalline, whereas, with fully heat-treated material the grain interiors and the boundaries are corroded, but a zone on either side of the grain boundaries remains unattacked, Fig. S (Plate LXXXIV). This material, too, has good resistance to stress-corrosion cracking in the fully heat-treated condition but we have not yet been able to correlate the type of attack with microstructure; it would be interesting to know whether alloy WZ3 shows any such correlation.

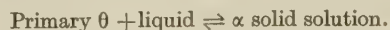
Professor Dr. G. WASSERMANN: \* The apparatus developed by Mr. Chadwick, Mr. Muir, and Mr. Grainger is clearly so reliable that it has been possible to make a notable reduction in the scatter of the results hitherto obtained for the stress-corrosion life of aluminium alloy specimens. This in turn has made it possible to obtain accurate stress/life curves from a smaller number of tests.

However, it is my opinion that the purely chemical attack on the samples under the conditions chosen was relatively severe, as evidenced by the very small difference in reduction of tensile strength between specimens subjected to corrosion only and those subjected to stress-corrosion. It is characteristic of stress-corrosion that cracks appear even when no corrosion attack is visible or any reduction in tensile strength occurs. In general, it is not stress-corrosion alone that is measured, but the combined damage due to ordinary corrosion and stress-corrosion.

It is interesting to note that the life of the specimens improved if the grains had an elongated shape. This recalls the effect of the position and extent of grain boundaries on the intercrystalline corrosion of zinc alloys. In this connection it would appear pertinent to determine whether the grain-boundary effect comes into play, if the corrosive medium is so weak that neither normal corrosion nor purely intercrystalline corrosion takes place.

Mr. L. E. STEELE,† M.Sc. (Member): I was interested to read Miss Day's paper, as I have investigated a similar alloy system, within the D.T.D. 683 specification, under conditions designed to approximate to those occurring in the liquid-metal head during the semi-continuous casting of large-diameter billets. The factors operating in the molten metal head are directly related to the casting technique employed and give rise to ideal conditions for the formation and growth of massive chromium-bearing constituents.

The investigation included the effect of iron, manganese, chromium, and titanium on the formation of primary  $\theta$ , particularly in the form of giant constituents (tending to the formula  $\text{CrAl}_7$ ). The ranges investigated were: Fe 0.10-0.35, Mn trace-0.35, Cr 0.10-0.25, Ti trace-0.05 wt.-%. Several laboratory-controlled melts were made comprising a combination of the above element ranges in a basic alloy of Si <0.05, Cu 1.35, Mg 2.65, Zn 6.0 wt.-%. Molten samples of each alloy were held for 16 hr. at a temperature a few degrees above the peritectic change:



The analysis of selected samples showed that titanium, as well as manganese and iron, can replace chromium in  $\text{CrAl}_7$ , the formulae approximating to  $(\text{Cr, Mn, Fe, Ti})\text{Al}_{6.5}$ .

The results obtained indicate that in this alloy type, the limit of primary  $\theta$  is considerably lower than that reported by Miss Day.

Mr. P. R. SPERRY ‡: Messrs. Chadwick, Muir, and Grainger are to be complimented on their valuable contribution to-

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‡ Research Metallurgist, Kaiser Aluminum and Chemical Corporation, Department of Metallurgical Research, Spokane 69, Washington, U.S.A.



wards a better understanding of the influence of composition upon the corrosion behaviour of aluminium alloys. I was particularly interested in the effects of chromium and manganese, since I have been conducting some studies on their influence upon the microstructure of wrought aluminium alloys. Some of my observations may have a bearing on the interpretation of resistance to stress-corrosion.

The authors have suggested that the principal effect of chromium on stress-corrosion behaviour is to alter the grain shape by furnishing greatly flattened or disc-shaped grains which appear elongated in the cross-sectioned metallographic samples. This argument applies well when propagation of intercrystalline attack is considered, but it fails to explain how the addition of chromium increases the incubation period which precedes initial crack formation. It would seem necessary to postulate some alteration of the metallurgical conditions existing within or around the grain boundaries which would increase their initial resistance to attack.

It has been observed that elongated grain shapes in alloys containing chromium or manganese are also accompanied by a dispersion of very fine precipitate particles aligned in bands in the same direction as the long dimension of the grains. Such precipitates, which have been shown by Chadwick, Muir, and Grainger in a previous publication,\* are formed at relatively high temperatures, resulting from the low solubility limits of chromium and manganese at the temperatures employed for ingot homogenization and for solution-treatment. The unevenness of the precipitate concentrations reflects the uneven distribution of chromium or manganese in the cast ingot structure. The precipitate continues to form over long time intervals and resists coalescence because of the pronounced sluggishness of diffusion of these elements. Therefore, it is remarkably stable and forms an intimate part of the metallurgical structure of the alloy. It is fairly certain that the bands of precipitate exert an influence on the rate of growth of recrystallizing grains in certain directions, and therefore help to promote elongated grain shapes, although other conditions of deformation and recrystallization probably contribute to grain shape also.

It is proposed that the dispersion of fine precipitate due to chromium or manganese has a predominant effect on the corrosion-resistance, while the influence of grain shape, which is incidental to the presence of such a precipitate, is only secondary. A mechanism for this effect is pictured as follows. Each small particle has an interface with the aluminium solid solution, which acts, in effect, like a grain boundary. The multiplicity and close spacing of these particles results in a large amount of randomly distributed interfacial phase-boundary area. Grain-boundary precipitation, which normally occurs during early stages of age-hardening and produces the localized heterogeneities responsible for intergranular corrosion, is then diminished because of the proximity of chromium or manganese particles along which ageing precipitation occurs. Thus, these particles act in somewhat the same manner as a grain refinement, with the further advantage of not being continuously connected.

There is circumstantial evidence for the proposed particle effect in the authors' data, which show a slight improvement in resistance to stress-corrosion of the alloy made with commercial-purity aluminium over that made with high-purity aluminium. Here, the insoluble iron constituents from commercial-purity aluminium furnished new interfacial area. The authors attributed this improvement in corrosion-resistance solely to the refinement in grain-size, but it was noted that the 0.25% manganese addition to the high-purity-base alloy effected a similar grain refinement without a concomitant improvement in resistance to corrosion. The manganese in the latter alloy was ineffectual because it was

not present in sufficient amount to effect a dispersion of fine particles. In general, a larger amount of manganese than chromium is required to achieve an equivalent effect.

DR. H. SUTTON, † C.B.E., F.R.Ae.S., F.I.M. (Member): Mr. Chadwick, Mr. Muir, and Mr. Grainger have probably had quite extensive experience of the extent to which alloys of the types on which they have been working recrystallize during final heat-treatment. They mention cold reduction to 0.1 in., annealing, and then cold rolling to finish at 0.05 in. If they examined their alloys to determine the extent of recrystallization in the condition as used in their experiments, perhaps they would comment on this, and give their views on the importance of recrystallization in final heat-treatment.

Reference is made in the paper to observations by Meikle on the advantages of more complete elevated-temperature ageing. A recent contribution by Martin ‡ confirms and emphasizes this point.

For interest, a plot has been made of the percentage loss of tensile strength in the accelerated test against percentage loss of strength in direct-stress tests as observed by the authors, but this did not appear to show any relationship.

It is valuable to have the authors' observations on mode of failure in simple tensile tests, presumably made under comparable conditions of loading, &c. These, coupled with performance under direct stress-corrosion tests, indicate that an intrinsic tendency to intercrystalline fracture is not a good feature in alloys required to withstand stress-corrosion conditions.

A very important feature to which the authors have aptly referred is that, under the conditions of their tests, the application of stress below that required to cause failure has led to no damage over and above that suffered by an unstressed specimen. It could be questioned whether in these circumstances the materials are really susceptible to stress-corrosion. A closely related matter is the somewhat disturbing inefficacy of many otherwise very useful methods of protecting light alloys against corrosion, in offsetting stress-cracking, or preventing it. There seems little doubt that corrosion influences the stress-cracking phenomenon, but that the greatest general advantage would be gained by improvement of the intrinsic resistance to stress-cracking of material of this general type.

Several years ago Bungardt § published some interesting observations on the benefits to be gained by delayed or restrained cooling of aluminium-zinc-magnesium alloys after solution-treatment by quenching in salt baths, &c., and in relation to failure under stress-corrosion conditions such treatments appeared to confer marked advantages. If the authors have experience of any such treatments, it would be of interest to have their views.

MR. CHADWICK, MR. MUIR, and MR. GRAINGER (*in reply*): The major criticism of our work relates to the use of sheet, on the grounds that this material is not in actual use except when protected by cladding. The reason for choosing sheet rather than extrusions is that rolling alone provides material uniform and constant in every respect. To develop an accurate method of testing in the first place, the availability of such uniform material is absolutely essential; otherwise it is impossible to differentiate between variations in behaviour due to the material and those associated with conditions of testing. By this selection of material and by rigorous control of the testing method, the stress/time curves reproduced in Figs. 2-5 (p. 167) were drawn up. Curves of this nature could not possibly have been obtained from material of such variable structure as that resulting from extrusion, except

\* R. Chadwick, N. B. Muir, and H. B. Grainger, *J. Inst. Metals*, 1953-54, 82, 75.

† Director of Materials Research (Air), Ministry of Supply,

London.

‡ A. J. Martin, *Metal Ind.*, 1956, 89, 511, 531.

§ W. Bungardt, *Aluminium*, 1944, 26, 129.



statistically by employing a very much greater number of tests. We agree wholeheartedly that the experiments described are only a beginning. They serve to demonstrate and prove the method of testing, and to show that relatively small differences in structure and composition lead to definite and definable differences in stress-corrosion behaviour. We certainly agree with Dr. Doyle and Dr. Farmery and with Messrs. Turner, Smith, and Cibula that the next important stage in work of this kind is to study extruded material, and we regret that we are not ourselves in a position to undertake this work.

In regard to the general acceptance of the results as expressed in stress/time curves and in the deduced safe levels of stressing where curves appear to be asymptotic to abscissæ, we are pleased to note Dr. Farmery's observations on the importance of the finding that no one curve crosses another, as providing a basis for the simplification of testing procedure. On the other hand, there seems to be a general lack of acceptance of a maximum safe stress or threshold stress deduced from these curves. Mr. Cibula favours the use of a log plot, giving a straight-line relationship. Mr. Sperry, however, draws attention to the appreciable amount of unstressed corrosion during 100 days' exposure in the cabinets, and this naturally lowers the apparent threshold stress. If conditions of stress-corrosion testing could be devised in such a way that the unstressed corrosion was very much reduced in amount, then it should be possible to get a figure for the minimum safe stress which might well be higher than that indicated by our stress/time curves. Since in practice the level of actual corrosion will vary, it is evident that there is no absolute value of minimum safe stress. Nevertheless, comparative levels can certainly be deduced, and we feel that Mr. Meikle's division of results into "good", "bad", and "indifferent" certainly does injustice to our results. However, we would agree that in the outdoor testing employed at the Royal Aircraft Establishment, with its widely varying degrees of temperature and humidity, Mr. Meikle's classification might well be about the best that could be achieved. We feel sure that in the room used by Dr. Champion, both temperature and humidity, as well as movements of air, are bound to be much less constant than in a small cabinet.

In the more general discussion of experimental methods, Dr. Champion criticizes the method of producing our metals. We cannot understand why he has assumed that we employed laboratory rolling mills. In fact, there was no mention of this in our paper, and all the sheets were rolled in the light-alloy plant. Dr. Farmery suggests that it would have been better to have carried out the tests on etched samples, so as to eliminate variables in the skin structure due to heat-treatment. A good deal of thought was given to this point, but we came to the conclusion that it was preferable to test the materials in the naturally rolled condition rather than after some artificially applied treatment, especially when the well-established effects of etching treatments on the fatigue properties of some of the heat-treatable alloys\* are borne in mind. However, before corrosion-testing, all samples were degreased by rubbing with a suspension of magnesia powder in water, which we have adopted as standard practice in all corrosion testing of aluminium alloys. Dr. Farmery also suggests that we should have carried out tests in bending, but we have, in fact, noted the many objections to such methods and their lack of reproducibility. Mr. Meikle expresses some uneasiness about the number of specimens which failed during loading, as indicated in Table IV, although these same alloys underwent tensile testing without premature failure. Possibly our description "Failed during loading" is slightly misleading, because this classification included all specimens which broke before the stress-corrosion test was

under way. The loading of the specimens in a tensile-testing machine, removal of ancillary gear, transfer to the corrosion-testing laboratory, installation in a cabinet, spraying, and setting of the clock recorder and trip, might take up to  $\frac{1}{2}$  hr.

There have been a number of comments on the corroding medium; both Dr. Farmery and Professor Wassermann discuss the suitability of salt spray, and the appreciable loss of strength of unstressed specimens after 100 days. We used 3% sodium chloride partly because this was the most commonly used medium in previous stress-corrosion-testing investigations. Obviously, if a long test has to be carried out, the smaller the actual corroding effect the better, and there may be some merit in using a weaker salt solution or even distilled water, as suggested by Mr. Cibula. If, however, a weaker salt solution is used, then evaporation or condensation is going to have a bigger effect, and the application of humidity control to keep the surfaces in a moist condition would be less effective. Indeed, if distilled water is to be used, there would seem to be no alternative but to spray the specimens continuously, which would greatly complicate the testing equipment, while for the testing of a large number of specimens simultaneously, the quantity of distilled water required would be quite substantial. Dr. Champion and Dr. Farmery compare the results of tests in salt spray and salt-peroxide solution, and Dr. Champion expresses a preference for salt spray. However, salt-peroxide solution certainly seems to yield a more positive indication of susceptibility to intercrystalline attack and, of course, it has the merit of giving a useful result after a very short period of immersion.

A great many contributions have been made on the compositional and related structural effects. Miss Day's work seems to be in conformity with our general findings on the effects of copper, chromium, and manganese, the first two elements tending to favour general precipitation and thus minimizing the potential effects at grain boundaries which lead to intercrystalline weakening. Miss Day regards manganese as suppressing the effect of copper, but our own observations seem to show that with copper and chromium already present a small manganese addition improves resistance to stress-corrosion. Dr. Champion compares results quoted in Table IV (p. 166) for alloys WZ7 and WZ8, and suggests that the higher-copper alloy WZ8 has the greater stress-corrosion susceptibility when the beneficial effect of iron is taken into account. In fact, on the direct comparison of times-to-failure, the higher-copper alloy is slightly better, although we would not regard these differences as significant. We have no evidence that the small variation in iron content is significant at this level, and since, in any case, we do not know the magnitude of its effect, we cannot see the justification for assuming that the increased copper has a compensating adverse effect. Indeed, we feel that deductions of this kind would be quite unjustified, even after the most careful rechecking of iron contents on the samples in question. We would, however, agree with his deductions from the figures reproduced in Table A as to the beneficial effects of iron where this element is increased by about ten times. The improved stress-corrosion behaviour of alloys with a commercial-purity base is clearly associated with either iron or silicon, and general metallurgical evidence would seem to show that iron is the desirable constituent, as Mr. Sperry also indicates.

On the question of stress-corrosion in relation to grain-boundary structure, Miss Day advances the by now classical theory that denuding of grain boundaries is the main mechanism, and this would be generally accepted. We have expressed the view that the anodic condition of grain boundaries so produced in the ternary alloys accounts for rapid failure under stress, but that when copper is present the grain centres may become even more anodic than the boundaries. Dr. Champion wonders why, if this is so, stress-corrosion fractures should invariably be intercrystalline. In fact, it

\* H. Sutton and W. J. Taylor, *J. Inst. Metals*, 1934, 55, 149.



must be presumed that when copper is present micro-currents flow from the material of the grain peripheries into both grain centres and grain boundaries. The anodic areas at the boundaries are narrow, and therefore penetration is deep, whereas on the larger area at the grain centre corrosion takes the form of a shallow depression. The boundaries are therefore weakened to a greater extent. We agree with Dr. Farmery that this could be explained by a levelling out of potential differences due to more general precipitation when copper is present.

Referring to grain-boundary shape, both Mr. Cibula and Mr. Sperry point out that the length of path in the transverse direction, where it has to circumvent the elongated grains, as in Fig. 21 (Plate XXX), cannot really explain the beneficial effect, since all the evidence is that as soon as intercrystalline cracking begins it rapidly spreads across a specimen irrespective of structure. However, if one compares Figs. 20 and 21 (Plate XXX) it will be apparent that with the equiaxed structure there are many grain boundaries cutting the surface where stress-corrosion could start, and the initial forming and deepening of a notch can readily occur without hindrance. With the elongated grain structure shown in Fig. 21, there are fewer points for initiation of attack, and in most cases a crack will be diverted into a plane parallel with the surface before it has proceeded far, so that the formation of a notch sufficiently deep to cause appreciable stress-raising is likely to take a very much longer time. This explanation would seem to be in accordance with Mr. Cibula's view that notch-brittleness and stress-corrosion susceptibility are related.

A number of contributors, including Dr. Farmery and Mr. Sperry, have drawn attention to the investigations of Dix, who put forward evidence that in the chromium-bearing alloys the grain-boundary precipitate differs from that in chromium-free alloys, so accounting for differences in stress-corrosion behaviour. On the other hand, Mr. Smith, Dr. Doyle, and Dr. Farmery all point out that when testing is carried out in the short-transverse direction, evidence for the beneficial influence of chromium is inconclusive and sometimes conflicting. This seems to support the view that grain-boundary configuration is the major factor. The evidence of grain-boundary differences appears to be based entirely on studies of microstructure, and there is no positive experimental work relating these differences to stress-corrosion behaviour. It is also worth re-emphasizing that comparison of the stress curves in Figs. 2-5 shows that the effect of chromium addition is to produce a moderate raising of stress levels for fracture in a given time, whereas earlier bend tests employing a "go"- "no go" type of criterion have given an exaggerated impression of the effect of chromium. Mr. Sperry refers to banded structures associated with the precipitation of chromium and manganese compounds, which we described in an earlier publication. If such banded structures are present, they must be a good deal finer and less easily detected than in the aluminium-magnesium-silicon alloys, and it is surprising that they have not been revealed in Miss Day's investigation.

In the previous work we invariably found that the banding was quite independent of the recrystallized grain structure, and we never encountered elongated grain shapes in the recrystallization of material having a banded structure already present. We should be interested to know whether Mr. Sperry has observed such an effect.

Mr. Sendorek refers to the low tensile-strength figures on alloys containing more than 7.4% Mg+Zn, and suggests that intercrystalline cracks were already present in the test-pieces. This may well be so, for in some of the ternary alloys based on high-purity aluminium, Hérenghuel has shown that quenching stress alone is sufficient to cause fracture.

Dr. Farmery refers to our observations on the exfoliation of Series III alloys in the salt-peroxide test. These observations were purely incidental to the investigation, and we have not done sufficient work on this subject to comment on the factors influencing exfoliation. Certainly, however, we would say that exfoliation occurs with all types of grain structure, and it is quite contrary to our experience to suggest that equiaxed structures are immune from it. At one stage we experienced exfoliation on the shoulders at the upper ends of test-pieces during stress-corrosion testing. This was associated with condensation in this area due to the conduction of heat from the upper ends of the test-pieces via the dash-pot assembly into the colder room atmosphere. It disappeared when we fitted the transparent plastic covers, as shown in Fig. 22 (Plate XXXI). It was not, however, possible at the time to follow up these observations.

Under our conditions of heat-treatment, all the sheet specimens were obtained in a fully recrystallized condition. In the alloys containing chromium or manganese, it should be possible by giving a final rolling reduction of less than about 10%, and keeping the heat-treatment temperature low, to avoid recrystallization. We have made no observations on susceptibility to stress-cracking in structures so obtained, and we cannot therefore answer Dr. Sutton's very interesting question. As Mr. Smith and Dr. Doyle have pointed out, and Hérenghuel and others showed many years ago, internal stresses induced by quenching may greatly increase the apparent susceptibility to stress-corrosion, and we would agree with Dr. Sutton that measures such as those suggested by Bungardt would be beneficial, provided that adequate mechanical properties could be achieved.

*Miss DAX (in reply):* In reply to Dr. Turner, I can only say that the boundary which I determined for the primary aluminium field has been found in practice within my own Company to provide a satisfactory guide to acceptable composition limits.

I was interested to find that Mr. Steele had carried out a similar investigation, and I hope that he will publish his results in more detail. His practice of holding his melts for 16 hr. at a temperature just above that of the peritectic reaction approximates far more closely to conditions of equilibrium than my own conditions of slow cooling, and this accounts for the lower limits of his primary  $\theta$  field.



## Discussion

## The Metallurgy of Niobium\*

Dr. B. B. ARGENT,† B.Met. (Student Member): Niobium has several potentially useful properties, e.g. a high creep-strength: weight ratio, good acid corrosion-resistance, and compatibility with many liquid metals.

Two factors prevent its effective utilization: (1) the high cost of metallic niobium, and (2) its poor oxidation-resistance.

## Cost

Three possible methods of making the use of niobium more attractive economically are:

(1) To stimulate a large demand for the metal. It seems likely that the price would fall if more economic large-scale production methods could be employed for both ore concentration and extraction.

The use of niobium in steels has not advanced much beyond its introduction as a stabilizing element in stainless steels and as a constituent of many creep-resisting austenitic steels. In the past, research work has probably been held up by restrictions on niobium as a strategic material, but since the United States has ceased to stock-pile niobium,

tantalum is required. One can also visualize certain other cases where the presence of tantalum in large quantities might make a part too heavy. However, for many purposes it should be possible to use niobium and tantalum, in the proportions in which they occur in the extracted mixed oxides, as a basis for making alloys. For example, we have carried out some simple corrosion tests on niobium-tantalum alloys and have found that under our experimental conditions there is really no significant difference between the corrosion-resistance of the alloys and that of the pure metals (see Table A).

The alloys examined could all be produced by the reduction of the mixed oxides obtained from existing ore bodies. Furthermore, some of the ores are sufficiently rich in niobium for there to be only a small weight penalty due to the presence of the denser tantalum.

## Oxidation-Resistance

The improvement of the oxidation-resistance of niobium presents a difficult problem. American workers‡ report that

TABLE A.—Corrosion-Resistance of Niobium-Tantalum Alloys.  
Rate of corrosion expressed in in./year. Specimens corroded at 15°–20° C. for 21 days.

Corrodent	HNO <sub>3</sub>	50% HNO <sub>3</sub>	1% HF + HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	10% H <sub>2</sub> SO <sub>4</sub>	HCl	5% NaCl	20% NaOH	NH <sub>4</sub> OH
Pure Ta	0.0013	0.0015	0.0037	0.0015	0.0015	0.0002	0.0029	0.0005	0.0003
Alloy:									
1:1	0.0007	0.0021	0.0038	0.0019	0.0022	0.0000	0.0000	0.0008	0.0001
1:4	0.0000	0.0000	0.0025	0.0037	0.0000	0.0000	0.0002	0.0004	0.0005
1:6	0.0004	0.0002	0.0057	0.0002	0.0000	0.0000	0.0000	0.0012	0.0086
1:10	0.0000	0.0000	0.0041	0.0000	0.0020	0.0000	0.0009	0.0025	0.0000
Pure Nb	0.0001	0.0034	0.0122	0.0042	0.0002	0.0032	0.0021	0.0040	0.0004

the supply situation has eased considerably and much research could now be done. In Sheffield a certain amount of work is being carried out on the use of niobium as an addition to relatively low-alloy steels. This study includes comparatively low-carbon iron-chromium-niobium alloys and ferritic steels containing approximately 0.2% carbon. The results obtained so far seem to indicate that quite good age-hardening alloys may be developed.

A large-scale demand for ferro-niobium might quite easily lead to a general decrease in the cost of niobium.

(2) To improve methods of production of pure niobium. The possible methods have been critically reviewed in three papers by U.K.A.E.A. workers.‡ One of the tentative conclusions was that the production of niobium by a chlorination process, using ferro-niobium as a starting material, was a commercially attractive process. It would be interesting to know whether this is being developed on a commercial scale and, if so, whether it will in fact be capable of producing a much cheaper metallic niobium.

(3) To employ niobium-tantalum alloys instead of pure niobium. One stage common to all the extraction processes proposed for niobium is the separation of niobium from tantalum. It is not apparent why this is always necessary. Certainly for atomic-energy purposes niobium metal free from

titanium, aluminium, and chromium all increase its oxidation-resistance and that a combination of titanium and chromium is particularly good. One problem is likely to remain as regards some of these alloys, namely to produce a workable material.

We also found that aluminium enhanced the oxidation-resistance of niobium and that this effect increased with aluminium content up to 15–20 at.-%, but Mr. B. S. Pearcey at Sheffield has determined the solubility of aluminium in niobium as less than 3 at.-%. The alloys high in aluminium are very brittle. Micrographic work indicates that great care is necessary in the interpretation of the microstructures. American workers have reported that a 5 at.-% alloy is in fact a solid solution. A grain-boundary precipitate appears in our alloys of this composition which might be interpreted as an over-etched grain boundary. However, with lower percentages of aluminium it is evident that there is, in fact, a change to a discontinuous grain-boundary precipitation.

Niobium-tantalum-base alloys may also possibly provide oxidation-resistance at high temperatures. One niobium-tantalum-titanium-aluminium alloy investigated shows quite good qualities in this respect.

Fundamental work on the oxidation of niobium alloys is being undertaken at Sheffield in an attempt to understand

\* Joint discussion on papers Nos. 1755–1759 (*Journal*, this vol., pp. 367–392) held in London on 1 May 1957.

† Metallurgy Department, University of Sheffield.

‡ A. B. McIntosh and J. S. Broadley, *Extraction and Refining of the Rarer Metals (Inst. Min. Met.)*, 1957, 272.

B. R. Steele and D. Geldart, *ibid.*, p. 287.

G. K. Dickson and J. A. Dukes, *ibid.*, p. 253.

§ S. J. Paprocki and J. T. Stacy, *Battelle Memorial Inst. Rep. BMI-1443*.

the mechanism of protection. We are considering the desirability of investigating coatings other than oxides.

#### Alloying Behaviour

Very little is known about the alloying behaviour of niobium. In an attempt to gain some insight into the problem, Mr. Pearcey has attempted to determine the heats of formation of several alloy systems by a method developed by Dr. O. Kubaschewski at the National Physical Laboratory. Of the 12 systems tried (including niobium with Fe, Co, Cr, Mn, Pb, Sn, or Bi), only two proved amenable to the method; these were the systems with aluminium and nickel. Work has been concentrated on the niobium-nickel system, as

stimulus for research into practical problems. Niobium is, however, interesting from the point of view of general alloy theory, and there is a need for physical measurements on the alloys. As a contribution in this field we intend to measure the paramagnetic susceptibilities of certain niobium alloys.

Dr. H. J. GOLDSCHMIDT,\* F.Inst.P. (Member): In Dr. McIntosh's survey of possible lines of niobium-alloy development, a number of binary systems are reproduced (Fig. 1, p. 370), including niobium-iron, and he draws attention to the importance of iron as a strengthener by precipitation-hardening. I think the diagram shown is based on that of Eggers and Peter,<sup>†</sup> and it contains the Laves phase, but

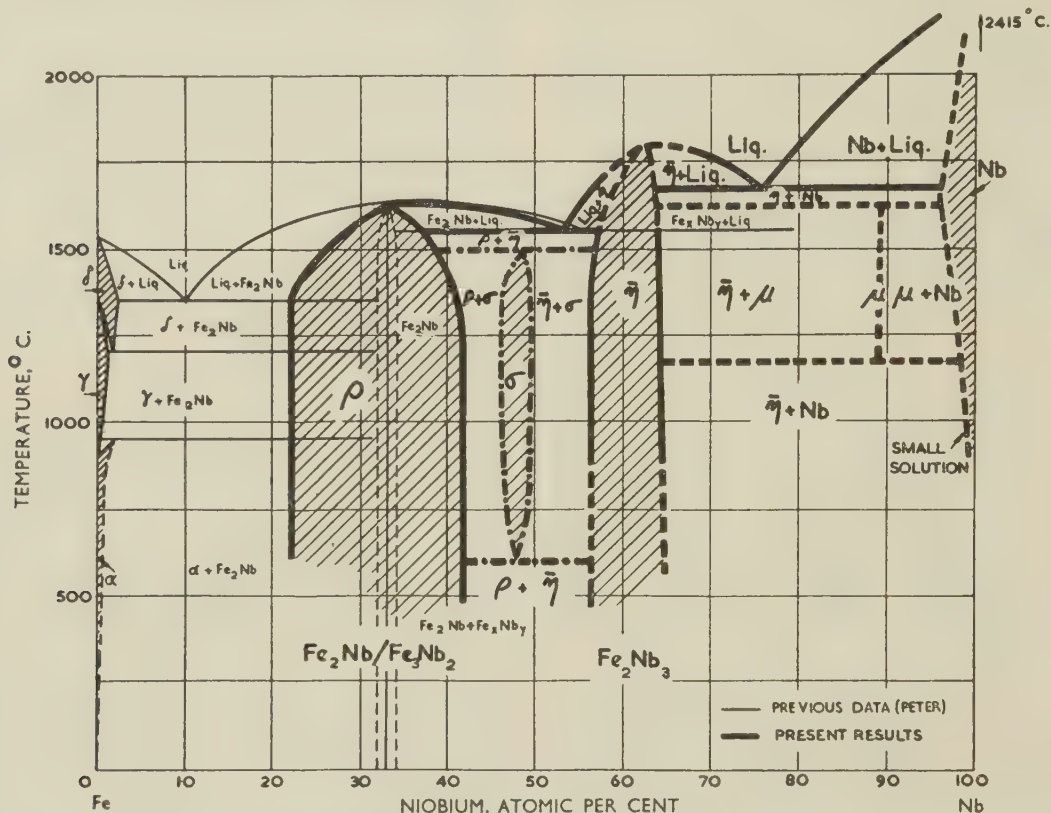


FIG. A.—Equilibrium Diagram of Niobium-Iron System.

the niobium-aluminium system presents several practical difficulties.

It would have been interesting to compare the heats of formation of the Laves phases  $\text{NbFe}_2$ ,  $\text{NbCr}_2$ ,  $\text{NbMn}_2$ ,  $\text{NbCo}_2$ , and also the limiting heats of solution of these elements in niobium. The overall object of the work has, however, not been attained owing to the experimental difficulties. Only in the case of nickel and aluminium did the reaction between the powdered metals proceed to completion in a sufficiently short time.

We have investigated the copper-niobium system with a view to the possibility of producing age-hardening alloys. Unfortunately, no alloys of this type exist at the copper-rich end and the system appears to be very simple, having limited terminal solid solutions with a peritectic reaction at the copper-rich side, approximately  $10^\circ\text{C}$ . above the melting point of copper.

The present interest in niobium is likely to provide a

there is a large gap at the niobium end, where only an indefinite compound " $\text{Fe}_x\text{Nb}_y$ " is indicated. We have investigated the niobium-iron system by X-ray methods, in an attempt to fill this gap, and as part of a wider study of the ternary system iron-niobium-silicon, and I should like briefly to mention some of the results, because I think they are new and are relevant.

There are three major intermetallic compounds. Starting from the niobium end: (1) A phase at about 40 at.-% iron, which has the  $\eta$ -carbide type of structure; (2) a high-temperature  $\sigma$  phase at about 50 at.-% iron; and (3) the Laves phase  $\text{Fe}_2\text{Nb}$ , but with a very wide homogeneity field extending from about 60 to 80 at.-% iron, and with major changes in lattice dimensions occurring within this range. Fig. A shows the modified niobium-iron diagram, though I should mention that several features are still tentative. The appearance of the  $\sigma$  phase was quite unexpected, although perhaps we should regard it as an analogue to the neighbouring iron-

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<sup>†</sup> H. Eggers and W. Peter, *Mitt. K.-W. Inst. Eisenforschung*, 1938, 20, 199.



molybdenum phase. There is some evidence for a further high-temperature compound very rich in niobium, but this still presents a problem. From the viewpoint of the age-hardenability of niobium the  $\eta$ -carbide type of phase would seem important, because on ageing this would be the phase in incipient precipitation from primary niobium; there is a small but definite solid solubility of iron in niobium metal, which increases with temperature, and which we have observed from a lattice-spacing decrease through the smaller iron atom. The appearance of this  $\eta$  phase in direct equilibrium with niobium also seems to have other implications, because an iron niobide with  $\eta$ -carbide structure is likely to be readily intersoluble with the large family of other  $M_6C$ -type

ium and silver. These are likely to form extensive solutions, although the electronic differences would tend to favour compound formation.

Very little is known of the niobium-aluminium system, and I suggest that this deserves high priority in investigation, for the alloys may also possess a high oxidation-resistance. In Fig. B iron is seen to have a difference of  $-13.6\%$ , and probably Dr. McIntosh refers to it as "in a borderline position" because it is near Hume-Rothery's critical value of  $15\%$ ; but I wonder whether this rule can be applied here, as compound formation and insolubility in niobium already occur with much smaller size differences.

It may perhaps help to give (Fig. C) a broad survey of all

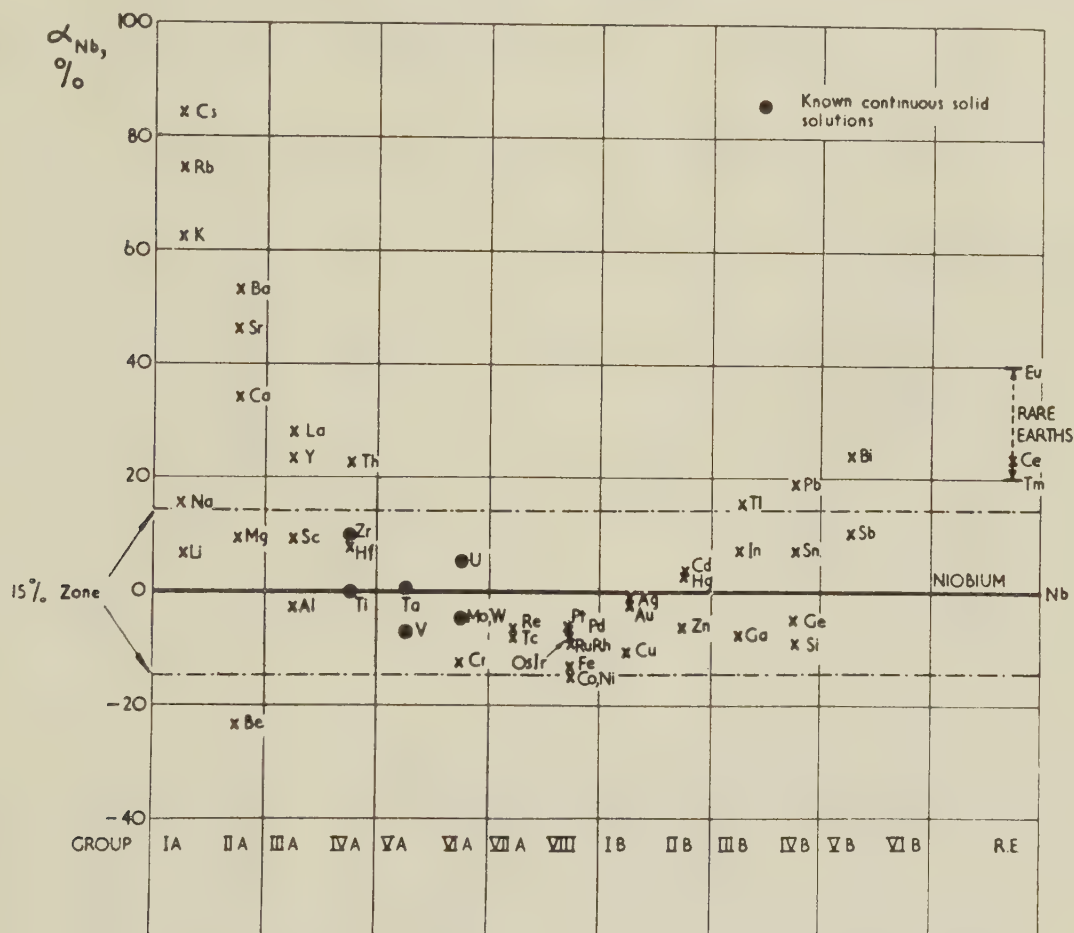


FIG. B.—Percentage Difference Between Atomic Radius of Various Elements and that of  $\alpha$ -Niobium.

compounds isomorphous with it, including carbides, nitrides, and oxides.

Referring briefly to the ternary iron-niobium-silicon system, the diagram so far derived proves to be extremely complex, particularly in the niobium corner, and there are a number of ternary compounds. One feature is a large solubility of silicon in the Laves phase.

To turn to some of the more general points in Dr. McIntosh's paper, a useful first approach in niobium-alloy selection lies in the atomic-size factor, and Fig. B shows the difference between the atomic radius of various elements and that of niobium. This demonstrates the conditions necessary (but not sufficient) for solid-solution formation in niobium; clearly the close proximity of titanium and tantalum is to be noted, but, rather significantly, also the favourable sizes of alumin-

the binary systems, as far as they are known, of niobium with transition metals. This is arranged according to the Periodic Table and is intended to show the trends in solid-solution and compound formation (as well as the gaps inviting further research). Diagrams of very great interest seem to be those, such as niobium-zirconium and niobium-uranium, having miscibility bays which open out within complete solid solution fields, as these systems are likely to give rise to new types of hardenable niobium-base alloys, in which joint precipitation of solid solutions and of intermetallic compounds could be made to occur. The same applies to the miscibility bays which can confidently be predicted to occur in certain ternary systems, such as niobium-chromium-molybdenum, or in general in Nb-A-B systems, where Nb-B and A-B are fully intersoluble, but Nb-A is not.

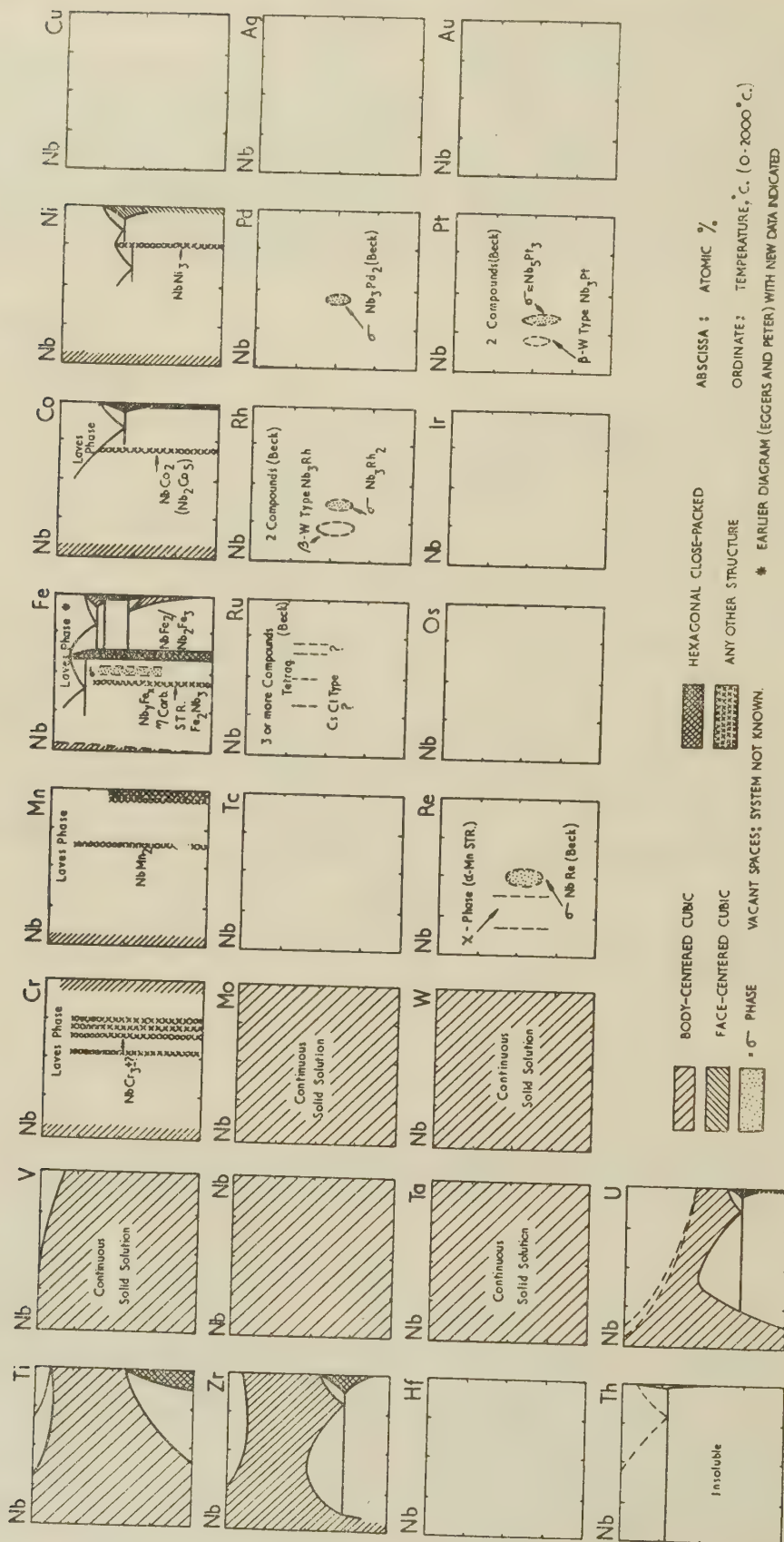


FIG. C.—Binary Systems of Niobium with Other Transition Metals Arranged According to the Periodic Table.



Finally, with reference to oxidation-resistance, may I make one important addition to Dr. McIntosh's survey of potentially useful niobium-base systems, namely niobium-silicon. I should refer here to the published work of Dr. Knappont,\* with which our own results show fair agreement. The niobium silicides are, I think, of special interest in giving high-temperature oxidation-resistance. Some curious effects can be produced, and one surprising result we have found is that the oxidation-resistance in air can be made much higher at 1200° than at 1000° C. This improvement can be directly related to the crystal structure of the oxide film formed and, without going into details, this seems to corroborate the point that niobium alloys may be so "designed" as to give structurally adaptable protective films, in which, for instance, phase transformations amongst the various forms of niobium oxide (including the high- and low-temperature forms of Nb<sub>2</sub>O<sub>5</sub>) can be prevented, and the more resilient structures stabilized.

Dr. M. VAN LANCKER,† F.I.M. (Member): Knowledge of the phase diagrams of niobium with other metals can be supplemented to only a very small extent by speculations based on alloy theory, but atomic thermodynamics, developed in the manner previously described, make possible more substantial advances in a shorter time.

Some essential variables have to be measured: (1) the entropy of fusion of the pure solvent (Nb) and of the various solutes (Zr, Mo, Pd) classified according to their atomic number. Special attention should be paid to the entropy of fusion of fission products: Sr, Y, Zr, Nb, Mo, Ru, Rh, of the rubidium group, and Cs, Ba, La, Ce, Pr, and other rare-earth metals of the caesium group. These values are also of importance in zone-melting and pyrometallurgical studies in relation to fuel reprocessing.‡ § (2) The segregation coefficient,  $A_0$ , should be measured or calculated at both ends of the diagram.  $A_0 = (N_{d(sol.)} : N_{d(liq.)})_0$ ;  $N = \text{at.-%} : 100$ .

Dr. McIntosh has reproduced some binary phase diagrams. It will be shown that these can be interrelated, using the following formulæ. On calculating the entropy characteristic  $Y$  of the solvent ( $S$ ) at the melting point of the pure solute ( $d$ ), it can be demonstrated that:

$$Y_S (\text{for pure } d) = \frac{RT_{Md}}{T_{MS} - T_{Md}} \cdot \ln A_{0,d} (\text{of the system } d - S) \quad (1)$$

$$= \Delta S_{MS} - \Delta c_{pS(T_{Md})} \left( 1 - \frac{T_{Md}}{T_{MS} - T_{Md}} \cdot \ln \frac{T_{MS}}{T_{Md}} \right) + b_{S(liq.)} X_{S(\text{pure } d)} \quad (2)$$

$T_{Md}$ ,  $T_{MS}$  are the absolute melting points of the solute  $d$  and the solvent  $S$  ( $= \text{Nb}$ ), respectively.

$R = 1.987 \text{ cal./}^\circ\text{C.}$

$\ln =$  Napierian logarithm.

$A_{0,d}$  = segregation coefficient in the region of the melting point of the pure solute  $d$ , i.e. for  $N_d = 1$ , written as follows:  $A_{0,d(S)}$ .

$\Delta S_{MS}$  = entropy of fusion ( $M =$  melting) of the solvent  $S$ .

$\Delta c_{pS}$  = difference between the molar heat capacities of the liquid pure solvent ( $S$ ) and of the solid solvent ( $S$ ).

$b_{S(liq.)}$  = interaction coefficient of  $S$  atoms with  $d$  atoms in the liquid state along the liquidus at the melting point of the pure solute.

$X_{S(\text{pure } d)}$  = interaction characteristic of the solvent at the melting point of the pure solute.

The general formula giving  $X_S$  is:

$$X_S = \frac{N_{d(liq.)}^2 - r_{bS} N_{d(sol.)}^2}{\Delta T} \quad (3)$$

At the melting point of the pure solute:  $N_{d(liq.)} = N_{d(sol.)} = 1$  and  $\Delta T = T_{MS} - T_{Md}$ . Therefore, the  $X_S$

value in equation (2) is  $\frac{1 - r_{bS}}{T_{MS} - T_{Md}}$ . In general,  $r_{bS} \approx 1$ , so that  $X_{S(\text{pure } d)} = 0$ .  $r_{bS} = b_{S(sol.)}/b_{S(liq.)}$ , i.e. the interaction coefficient of the solvent along the solidus at the melting point of the pure solute ( $b_{S(sol.)}$ ) divided by the interaction coefficient of the solvent along the liquidus at the same melting point. We will assume in the first instance that  $r_{bS} = 1$ ; formulæ defining  $r_{bS}$  as a function of the dimension factor  $\tau$  (atomic diameter of solute/atomic diameter of the solvent) permit a better approach to the value of  $A_0$ .

In order to determine the segregation coefficient  $A_0$  on one side (Nb) of a binary phase diagram (liquidus, solidus), we take the entropy characteristic  $Y$  of the other component and equate this with the entropy of fusion of that component.

The segregation coefficient  $A_{0,Nb}$  resulting from the addition of tantalum (Ta) is given by the equation:

$$Y_{Ta} = \frac{RT_{MNb}}{T_{MTa} - T_{MNb}} \cdot \ln A_{0,Nb} = \Delta S_{MTa} \quad (4)$$

Equation (4) may be completed with the help of  $\Delta c_p$ , according to equation (2):

$$T_{MNb} = 2741^\circ \text{ K.}; T_{MTa} = 3253^\circ \text{ K.}; T_{Ta} - T_{Nb} = 512^\circ \text{ K.}$$

$$\Delta S_{Ta} = 1.9 (\text{or } 2.1) \text{ cal./deg. g.-atom}$$

$$\ln A_{0,Nb} = 2.1 \text{ cal./deg. } 512^\circ / R \cdot 2741^\circ = 0.198$$

$$A_{0,Nb} = 1.22 = N_{Ta(sol.)}/N_{Ta(liq.)}$$

The molar depression of the liquidus in the region of pure niobium produced by the addition of small quantities of tantalum is thus:

$$\left( \frac{\Delta t}{m} \right)_{0, \text{liq.}} = K_f (1 - A_{0,Nb}) = -0.22 K_f \quad (5)$$

where  $K_f$  is the cryoscopic constant of niobium

$$= \frac{R \cdot 2741 \times 92.91}{2.30 \text{ cal. deg.}^{-1} \times 1000} = 220.$$

$$\text{Then } \left( \frac{\Delta t}{m} \right)_{0, \text{liq.}} = -0.22 \times 220 = -48.4.$$

The molar depression of the solidus in the region of pure niobium is then:

$$\left( \frac{\Delta t}{m} \right)_{0, \text{sol.}} = \frac{-48.4}{1.22} = -39.6 \quad (6)$$

Taking as an example the material supplied by Messrs. Johnson, Matthey and Co., Ltd., containing 1.9 wt.-% tantalum, which was used in the experiments by Mr. Schofield, we define the effect of tantalum on the melting point of niobium as follows:

If  $m$  = the number of gramme-atoms of tantalum in solution in 1000 g. of niobium = 0.1072:

$$\Delta t \approx -39.6 \times 0.1072 = -4.23^\circ \text{ C.} \quad (6a)$$

The effect of tantalum (1.9 wt.-%) on the solidus of the niobium-tantalum diagram is thus a negative depression of the melting point. Assuming:

$$t_{MNb(\text{pure})} = 2468^\circ \text{ C., then } t_{\text{solidus (Nb-1.9 wt.-% Ta)}} = 2468^\circ - (-4.23^\circ \text{ C.}) = 2472.2^\circ \text{ C.}$$

The  $\Delta t$  value (6a) is only about 40% of that given by Mr. Schofield. It is important to note that  $A_0$  has been established for an  $r_b$  value = 1. Further investigations are necessary. A useful experiment would be to allow liquid to form a deep axial hole in a cylinder of niobium (1.9 wt.-% tantalum) heated to 2472.2° C., and to establish the tantalum content of the liquid when it solidifies.

\* A. G. Knappont, *Nature*, 1955, 175, 730.

† Atomic Energy Consultant, Antwerp, Belgium.

‡ J. E. Antill, *Nuclear Power*, 1956, 1, 155.

§ M. van Lancker, "The Physical Chemistry of Pyrometallurgical Processes," 1957: Brussels (Centre d'Etudes pour les Applications de l'Energie Nucléaire).

If our calculations are correct, it should be found that:

$$N_{d(\text{liq.})} = N_{d(\text{sol.})} : 1.22 = 0.00986 : 1.22 \\ = 0.0081 \text{ or } 0.81 \text{ at.-% tantalum.}$$

This example is quoted to show how quite simple calculations can provide much information and give accurate results.

Let us now consider the influence of  $\Delta c_p$  in equation (2), when introduced into equation (4).

If  $\Delta c_{p\text{Ta}} = 0.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ , at the melting point of niobium, the entropy characteristic  $Y_{\text{Ta}}$  is given by:

$$Y_{\text{Ta (for pure Nb)}} = \Delta S_{M\text{Ta}} - \Delta c_{p\text{Ta}} \left( 1 - \left( \frac{2741}{512} \cdot \ln \frac{3253}{2741} \right) \right) \\ = 2.1 \text{ cal. deg.}^{-1} - 0.5 \times 0.092 \\ = 2.1 - 0.046 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (7)$$

The influence of  $\Delta c_p$  is slight and is masked by the low accuracy of the value of the entropy of fusion of tantalum.

The interrelationship of the diagrams in Dr. McIntosh's paper can be deduced from the following equations: the segregation coefficients ( $A_0$ ) in the region of pure niobium are calculated for the various solutes, arranged according to their atomic numbers. It has already been shown that for a given solvent (copper) and various solutes (Zn, Ga, Ge, As, Se, Br, Kr) of the copper family,  $A_0$  varies in a regular manner from 1 for copper to 0 for Br or Kr, and that at the melting point of pure copper ( $\ln A_0$ ) is a parabolic function of the atomic number of the solute. For Br,  $\ln A_0 = -\infty$ . The same rate applies to the solutes of the silver family. Periodic variations have been found in the region of the allotropic transformation points of uranium and zirconium. Some results have been published at the Argonne National Laboratory,\* but the  $Q_B$  value, termed the thermodynamic index quantity, has no strict thermodynamic interpretation. I have shown† that  $Q_B$  represents the difference between the partial molar free energy of the solute required for the extraction of 1 g.-atom of pure solute out of the  $\alpha$  phase and that required for the extraction of the same quantity out of the  $\beta$  phase, on the assumption that the activity coefficients of the solute in the region of the pure solvent are equal to unity. This is, of course, not the case, and it is better to use the more detailed equations given here; these should be supplemented by a special investigation of the  $r_b$  values given in equation (3). High-precision diagrams, such as those determined by Dr. Hume-Rothery, are essential; however, they should always be supplemented by considerations of thermodynamic compatibility, in the manner I have shown for the uranium systems,‡ and for the titanium-nickel§ and germanium-copper|| phase diagrams.

Let us consider the behaviour of niobium in the presence of fission products of the rubidium family, e.g. Zr (40), Nb (41), Mo (42), Ru (44). We take the entropy characteristics of these fission products  $Y_{\text{Zr}}$ ,  $Y_{\text{Mo}}$ ,  $Y_{\text{Ru}}$  ( $Y_{\text{Rb}}$ ,  $Y_{\text{Pd}}$ ) at the melting point of pure niobium:

$$Y_{\text{Zr}} = S(\ln \text{ in the region of pure Nb}) = \frac{RT_{M\text{Nb}}}{T_{M\text{Zr}} - T_{M\text{Nb}}} \cdot \ln A_{0, \text{Nb(Zr)}} \\ = \Delta S_{M\text{Zr}} + \omega_{\text{Zr}} \quad (7a)$$

$A_0$  is the value of the segregation coefficient in the region of pure niobium produced by the addition of (Zr),  $\omega$  is the  $\Delta c_p$  term given in equation (2), later supplemented by the influence of  $r_{bs}$ .

$$Y_{\text{Mo}} = \frac{RT_{M\text{Nb}}}{T_{M\text{Mo}} - T_{M\text{Nb}}} \cdot \ln A_{0, \text{Nb(Mo)}} = \Delta S_{M\text{Mo}} + \omega_{\text{Mo}} \quad (7b)$$

$$Y_{\text{Ru}} = \frac{RT_{M\text{Nb}}}{T_{M\text{Ru}} - T_{M\text{Nb}}} \cdot \ln A_{0, \text{Nb(Ru)}} = \Delta S_{M\text{Ru}} + \omega_{\text{Ru}} \quad (7c)$$

If  $\ln A_{0, \text{Nb(Zr)}}$  is known from previous calculations and experiments, then  $\ln A_{0, \text{Nb(Ru)}}$  is given by:

$$\ln A_{0, \text{Nb(Ru)}} = \frac{\Delta S_{M\text{Zr}}}{\Delta S_{M\text{Ru}}} \cdot \ln A_{0, \text{Nb(Zr)}} \cdot \frac{T_{M\text{Ru}} - T_{M\text{Nb}}}{T_{M\text{Zr}} - T_{M\text{Nb}}} \quad (8)$$

Equation (8) may be completed by the aid of  $\omega$  (equation (7)).

Knowing the segregation coefficient in the region of pure niobium produced by traces of ruthenium, we can draw the liquidus and solidus curves near the origin, using equations (5) and (6). The interrelationship of the diagrams is shown by equation (8). A more complete treatment of the thermodynamic aspect has been published elsewhere.¶ The basic features may be summarized as follows: (i) Complete entropy/interaction curves should be drawn for both solvent and solute; (ii) activity diagrams for classified solutes at different liquidus and solidus temperatures can be compared; (iii) segregation coefficients can be measured with great precision by the Darmonis-van Lancker method, using special cryoscopic equipment for very low molarities ( $m$ ) of the solute; from these values is apparent the periodic behaviour of ( $\ln A_0$ ) and also the parabolic laws can be established as a function of atomic number. These laws enable us to interpolate  $A_0$  values for systems of nuclear interest which are as yet undetermined. Zone-melting studies can be conducted with greater ease, especially in the case of reprocessing uranium-niobium irradiated materials. When high-temperature precision cryoscopy is impossible, spectrographic analysis along zone-melted bars will permit of the calculation of segregation coefficients. The same formulæ can be used to explain the physico-chemistry of pyrometallurgical processes employed in the reprocessing of neutron-irradiated fuels.

Dr. W. E. DENNIS,\*\* B.Sc., D.I.C. (Member): Of the new metals which have in recent years been proffered to the reactor designer, niobium probably bears the closest resemblance in its properties to what we normally regard as an engineering material: it is isotropic, it is non-toxic, and it does not melt below red heat.

Unfortunately, owing to its comparatively high neutron-absorption cross-section, this metal is not likely to find application in the natural-uranium-type reactors on which our immediate power programme is based. In the type of reactor to which it could most successfully be applied, liquid-metal coolants are almost certain to be used.

I have the impression that one of the major problems in successfully applying niobium may be the readiness with which it getters oxygen, and I do not feel that this point has received sufficiently detailed treatment in the papers. Dr. McIntosh reports (p. 369) that the presence of a small concentration of oxygen in liquid sodium or sodium-potassium alloy caused a significant increase in the corrosion rate. He also states that this corrosion can be reduced to acceptably low values by ensuring that the oxygen level is kept at a minimum, and that for this purpose it has been possible to design suitable cold-trap filters.

However, he leaves the following important questions unanswered:

(1) At how low a level, at various temperatures, does the oxygen content of the sodium have to be maintained to prevent significant corrosion of niobium?

(2) With a large engineering circuit, including valves, pumps, and heat-exchangers, what level of oxygen content is it reasonable to suppose can be maintained?

(3) Niobium oxides are very much more stable than sodium oxide; thus at some temperature the rate of oxidation of niobium in sodium will reach a level where the niobium can

\* A. E. Dwight, *Trans. Amer. Inst. Min. Met. Eng.*, 1956, **206**, 162.

† M. van Lancker, *Rapp. Centre d'Etudes Energie Nucléaire*, 1957.

‡ *J. Inst. Metals*, 1954-55, **83**, 538 (discussion).

§ *Ibid.*, 1955-56, **84**, 534 (discussion).

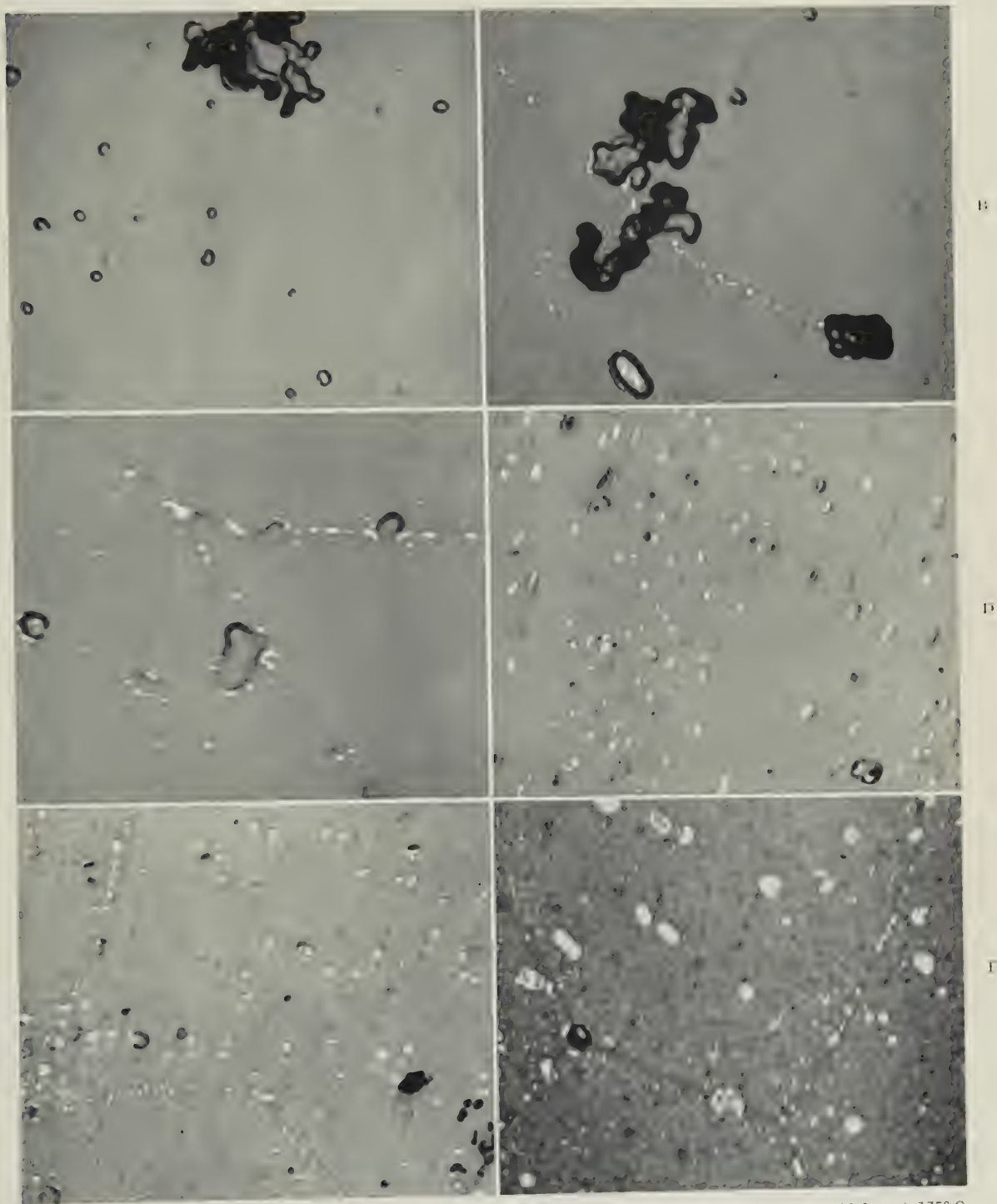
¶ Unpublished work.

¶ M. van Lancker, "De re metallica", 1956; Thesis, Univ. Paris, 1954.

\*\* Atomic Energy Department, General Electric Co., Ltd., Fraser and Chalmers Engineering Works, Erith, Kent.



## ELECTRON MICROGRAPHS OF ALUMINIUM-ZINC-MAGNESIUM-COPPER ALLOYS.

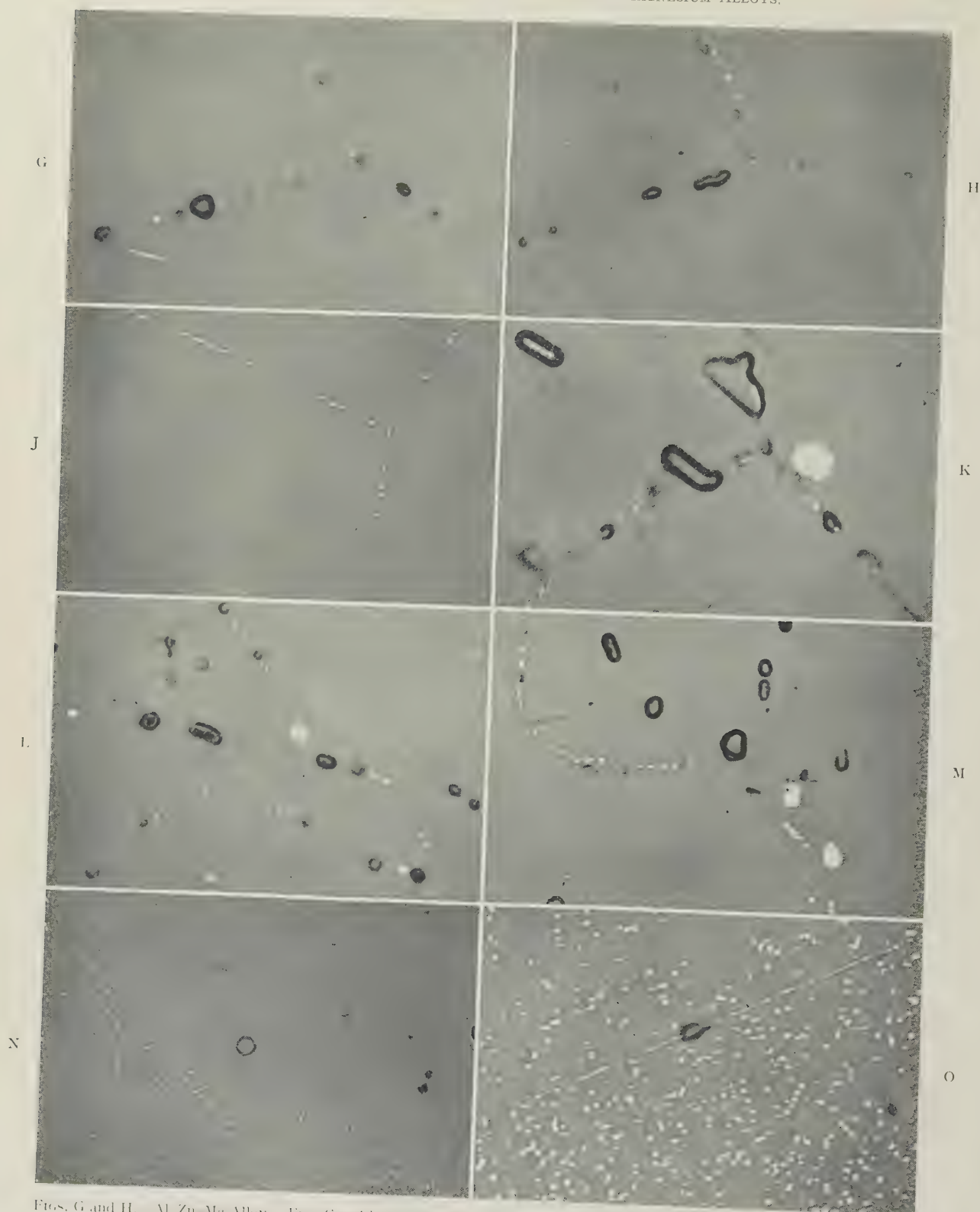


FIGS. A-C.—Al-Zn-Mg-Cu-Mn Alloy. FIG. A.—As quenched from 465° C.  $\times 15,000$ . FIG. B.—After 16 hr. at 135° C.  $\times 17,500$ . FIG. C.—After 48 hr. at 135° C.  $\times 23,500$ .  
 FIGS. D-F.—Al-Zn-Mg-Cu-Cr Alloy. FIG. D.—As quenched from 465° C.  $\times 14,500$ . FIG. E.—After 16 hr. at 135° C.  $\times 17,000$ . FIG. F.—After 48 hr. at 135° C.  $\times 23,500$ .

(Day)

[To face p. 552.

## ELECTRON MICROGRAPHS OF ALUMINIUM-ZINC-MAGNESIUM ALLOYS.



Figs. G and H.—Al-Zn-Mg Alloy. FIG. G.—After 16 hr. at 135° C.  $\times 18,500$ . FIG. H.—After 48 hr. at 135° C.  $\times 16,000$ .  
 Figs. J and K.—Al-Zn-Mg-Mn Alloy. FIG. J.—After 16 hr. at 135° C.  $\times 18,500$ . FIG. K.—After 48 hr. at 135° C.  $\times 20,000$ .  
 Figs. L and M.—Al-Zn-Mg-Cr Alloy. FIG. L.—After 16 hr. at 135° C.  $\times 17,000$ . FIG. M.—After 48 hr. at 135° C.  $\times 16,000$ .  
 Figs. N and O.—Al-Zn-Mg-Cu Alloy. FIG. N.—As quenched from 465° C.  $\times 12,000$ . FIG. O.—After 48 hr. at 135° C.  $\times 24,500$ .

(Day)



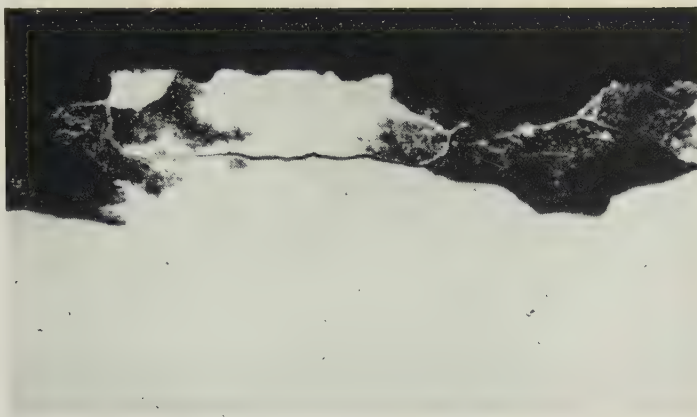


FIG. S.—The Tension Face of a Stressed Aluminium-Copper-Cadmium Extrusion Exposed for 1 year to a Marine Atmosphere.  $\times 250$ . (Farmery.)

### Discussion on Niobium

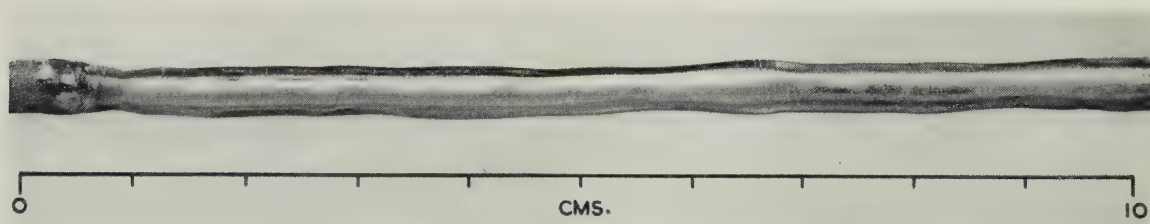


FIG. D.—Single Crystal of Niobium Produced by the Method of Electron-Bombardment Floating-Zone Melting. (Calverley.)

### Discussion on Welsh

#### PSEUDO-SUBGRAIN STRUCTURES IN ALUMINIUM.

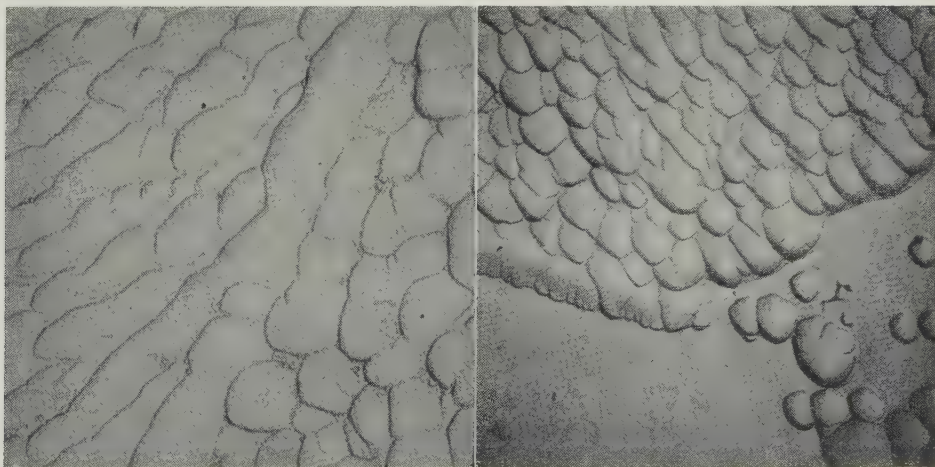
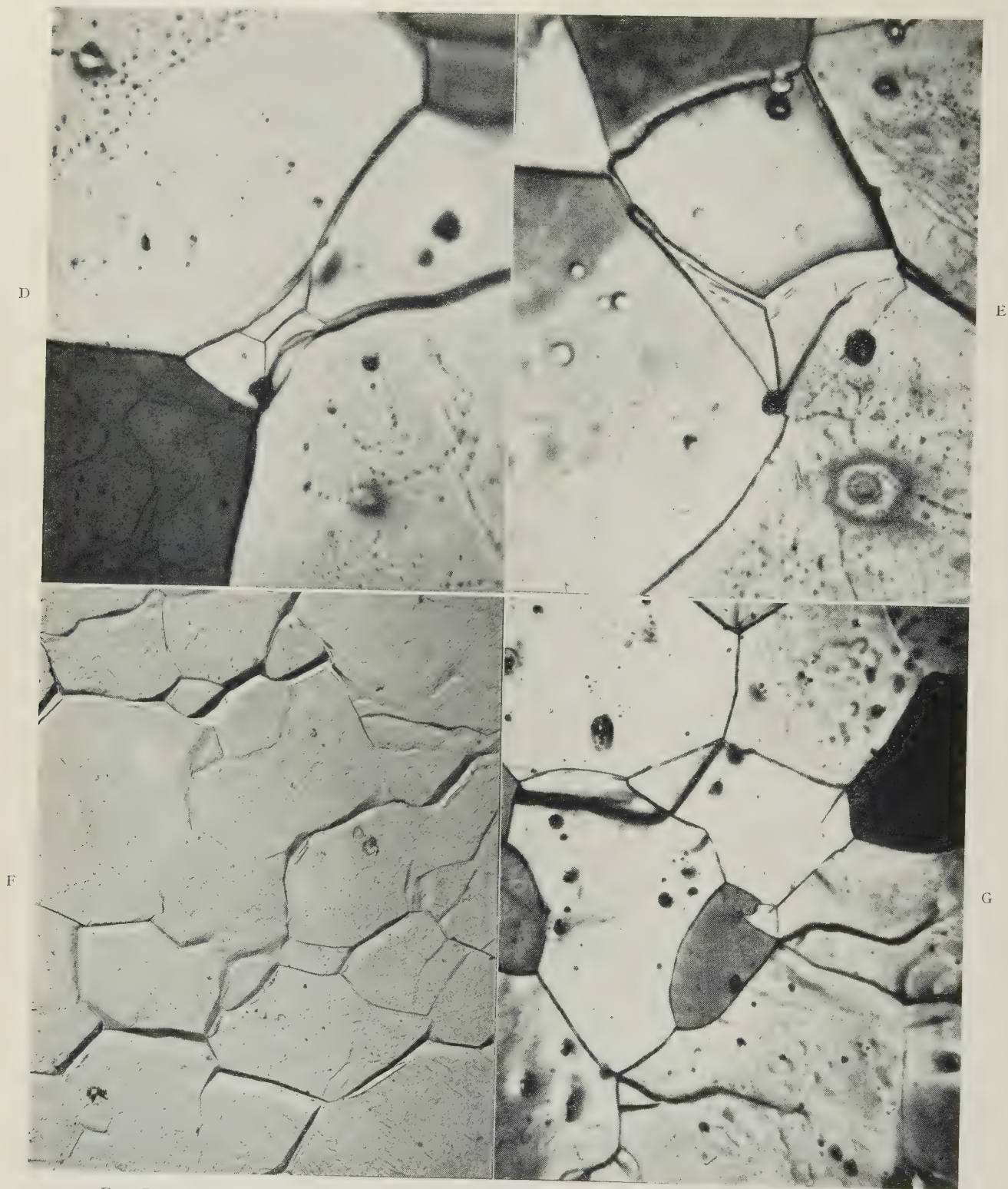


FIG. A.—Structure Formed by 4 Hours' Immersion without Applied e.m.f. in the Phosphoric Acid-Alcohol-Water Bath. Mean spacing of polygons 3500 Å.  $\times 16,000$ .

FIG. B.—Treatment as Fig. A. Structure fully developed only on one grain at ternary grain boundary.  $\times 12,000$ .

(Welsh's reply.)



FIGS. D and E.—Surface of a Test-Piece of Soft Iron after Creep at 750° C.  $\times 960$ .

FIG. F.—Electron Micrograph of Sub-Grains in a Test-Piece of Soft Iron Broken in Tension at 750° C.  $\times 4000$ .

FIG. G.—Surface of a Test-Piece of Soft Iron after Creep at 750° C.  $\times 240$ .

(Plateau, Crussard, and Constant)



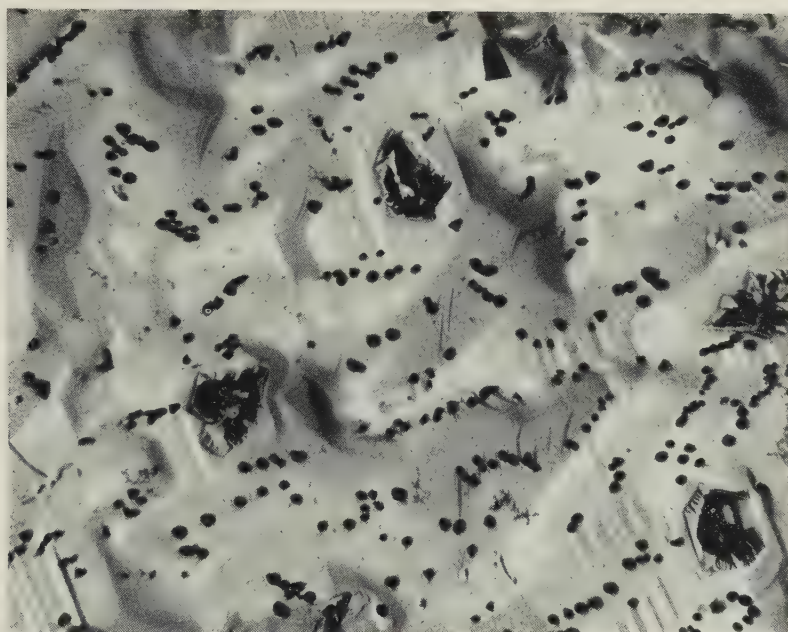


FIG. H.—Electron Micrograph of the Creep-Rupture Surface of a Test-Piece of Austenitic Steel Loaded to 4 kg./mm.<sup>2</sup> at 800° C. Showing carbides formed during creep and small particles of oxide formed after rupture.  $\times 4000$ .

*(Plateau, Crussard, and Constant)*

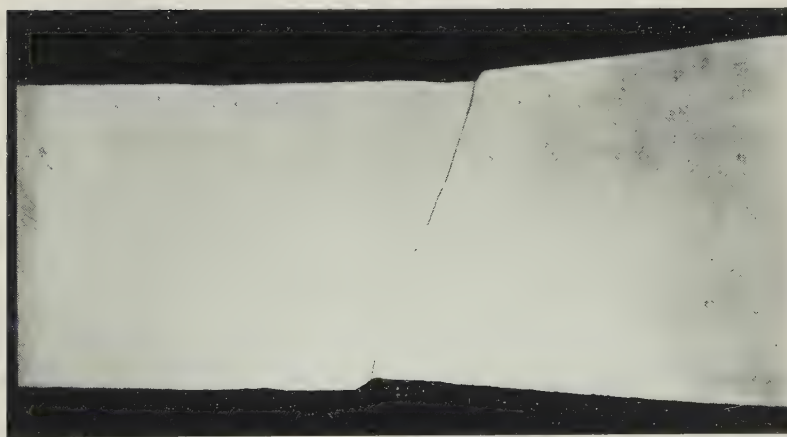


FIG. J.—Platinum Wire, 0.020 in. in dia., after Extension in Creep at 1400° C.  $\times 120$ . *(Chaston)*.





compete successfully with the cold traps in removing oxygen from the coolant. Furthermore, oxygen which has leaked into the circuit may react with the niobium before it reaches the cold trap. At what temperature is such a rate reached?

I should also be interested to know whether the authors of the papers consider that there is any likelihood of carbon being transferred from steel components in the sodium circuit to niobium used as a canning material, in view of the fact that niobium carbide has a free energy of formation per gramme-atom about twice that of the most stable carbide of chromium, and the fact that mass transfer of carbon has been observed in some sodium/metal systems.

Before the development work described in the present papers was carried out the American Fansteel Corporation had expended considerable effort on niobium and I should be interested to hear from the authors whether the American work on this metal has kept pace with our own, or if not whether the Americans view it with less favour from the point of view of reactor applications.

Finally, I should be most grateful if the authors could give us some rough figures for the present price of niobium per pound before and after fabrication into tubes. If this is not possible, could they at any rate place it in perspective relative to beryllium, zirconium, and other canning materials.

Dr. C. EDELEANU,\* M.A. (Member): Without wishing in any way to detract from the value of the work described in the papers, I wonder whether it would not be worth reconsidering the possibility of producing massive niobium by electrochemical means. What can be done now by powder metallurgy, even starting with impure powder, is impressive and no doubt we shall see equally rapid progress in the next few years. But would not everyone's task be made easier if advanced techniques could also be used in fused-salt electrolysis? Must we always end up with powder, and if so, can we not produce a powder less contaminated with oxygen and handled in such a way that it does not become contaminated?

This raises very interesting electrochemical problems which may be worth investigating further. One difficulty is that it is not easy to find out exactly what had already been tried out before it was decided to accept the powders in their present form. The real question is: Is there any theoretical reason why we cannot expect to produce massive, oxygen-free niobium by electrochemical means and would it matter greatly if it were slightly contaminated by halides if it were arc-melted afterwards?

Dr. O. KUBASCHEWSKI † (Member): The oxidation behaviour of niobium in air above 1000° C. seems to be determined largely by considerable compressive stresses which develop in the oxide layer, presumably owing to the high volume ratio of niobium pentoxide. Fifteen years ago we observed that a rather impure niobium formed a very protective film at 1250° C. which, however, became detached at the slightest provocation, exposing fresh metal surface to further attack. With the mechanism indicated by these results a linear oxidation rate is also compatible. It is therefore suggested that oxidation tests on niobium alloys should be carried out either with the temperature fluctuating or with mechanical agitation of the specimens.

In the circumstances it is difficult to propose suitable alloying elements to improve the oxidation-resistance. From the Wagner mechanism it is concluded that the diffusion rates in Nb<sub>2</sub>O<sub>5</sub> could be reduced by addition of metals of higher valency to niobium, but since MoO<sub>3</sub> and WO<sub>3</sub> also have high

volume ratios this way seems to be barred. One might, however, try adding metals of suitable volume ratio with a more exothermic heat of oxidation, forming oxides of the excess-semi-conducting type, such as Ti, Zr, Si, Al, Th, and Ca. Relatively large additions would probably be required to obtain substantial effects.

A minor point concerns the free energy of dissociation of 2NbO at 2000° C., which is given in the paper by Mr. O'Driscoll and Dr. Miller as 140 k.cal., but which is probably nearer to 107 k.cal. Otherwise the reduction of NbO<sub>2</sub> to NbO by hydrogen would be much easier than it actually is. Since the solubility of oxygen in niobium at 2000° C. seems to be of the order of 10 at.-%, a considerable increase of the dissociation energy must take place with decreasing oxygen concentration; this increase may be estimated to be approximately 10 k.cal./mole O<sub>2</sub>/power of ten in the concentration.

Mr. A. CALVERLEY, ‡ B.Sc.: All the work described in the papers has concerned polycrystalline niobium. Should the various authors' interests bring them to a study of single-crystal niobium, I should like to point out that this can be produced by electron-bombardment floating-zone melting.§|| At the request of Dr. K. Mendelssohn, of the Clarendon Laboratory, I recently tried to make a single crystal of niobium and found that this could be achieved without much difficulty. The crystal, illustrated in Fig. D (Plate LXXXIV), occupied approximately 7 cm. of a zoned length of 10 cm., and its diameter was non-uniform and approximately 4.5 mm. The power requirements were 1.4 kV., 100 m.amp., and the zoning speed 1.25 cm./min. I have not determined the crystal orientation, nor ascertained whether or not certain markings are slip lines or irregularities due to the solidification of the niobium after the passage of the molten zone.

Mr. Schofield has shown how the melting point of niobium varies with gas content. We have not measured the gas content of our specimen, and I should be most interested to see him carry out a melting-point determination on one of our crystals. To alter the melting point from the delightful value of 2468° C. would, however, be rather perverse!

The Admiralty are thanked for permission to make this contribution.

Dr. R. W. POWELL ¶: Mr. Tottle's paper contains, I believe, the first published values for the thermal conductivity of niobium. In the Physics Division of the National Physical Laboratory measurements of the thermal conductivity and electrical resistivity have been made over a limited range of temperatures for two samples of niobium obtained from Messrs. Johnson, Matthey and Co., Ltd.

The results obtained for these two properties and for the Lorenz function are given in Table B, where Tottle's values are reproduced to enable a comparison to be made.

Samples A and B contained 0.3 and 0.1% tantalum, respectively. Their initial resistivities at 20° C. were 16.9 and 16.2, compared with about 16.0 for Tottle's sample.

Using a comparative longitudinal heat-flow method, thermal-conductivity measurements were made on Sample B up to 236° C., after which the rod became seriously oxidized and the test was abandoned. The resistivity values shown for this sample are estimated values based on the room-temperature value.

The resistivity of sample A had been determined up to 1450° C. before the thermal conductivity was measured. The vacuum used would appear to have been insufficient, as the resistivity at 20° C. had increased to 17.7 after this treatment. Only a few thermal-conductivity observations were therefore

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‡ Services Electronics Research Laboratory, Baldock, Herts.

§ M. Davis, A. Calverley, and R. F. Lever, *J. Appl. Physics*,

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1956, 27, 195.

|| A. Calverley, M. Davis, and R. F. Lever, *J. Sci. Instruments*, 1957, 34, 142.

¶ Physics Division, National Physical Laboratory, Teddington, Middlesex.

made on this sample, determinations over as wide a temperature range as possible being deferred until a purer sample was available.\*

From the results presented in Table B, the electrical resistivity of sample *B* is seen to be 1–1.5% above Tottle's value. This is a relatively small difference and may be due to lack of annealing or to compositional variations. The values of the Lorenz function are likely to serve as a better basis for comparing the accuracy of the two sets of measurements. Whilst the N.P.L. values for the two samples agree to within about 1%, the values due to Tottle are about 6% higher. This suggests that there may be a real difference of about this order between the thermal-conductivity determinations of the two laboratories.

An uncertainty of the order of 5% in the thermal conductivity may not be of much concern, but I am prompted to ask if any other metals have been examined in the author's

ing significant quantities of oxygen could have been reduced by slow cooling, and it would be of interest to know whether the author has any information on this point.

It is worth recording that the binary phase diagrams containing niobium reproduced by Dr. McIntosh in Fig. 1 (p. 370) does not include the niobium-silicon system; phase diagrams for this system have been published by Knappton § and by Kieffer, Benesovsky, and Schmid.||

Mr. T. H. SCHOFIELD,¶ M.Sc., F.I.M. (Member): I should like to comment on Tables V and VI (p. 377) of Mr. Tottle's paper. The data presented in Table VI appear to me to be most unsatisfactory without further information on the impurity contents of the alloys. For example, the hardness numbers of two 10% tantalum alloys are stated to be 74 and 111 V.P.N., respectively, as compared with a hardness of 87 for the unalloyed niobium! Moreover, a hardness of 74 for

TABLE B.—*Thermal Conductivity, Electrical Resistivity, and Lorenz Function of Niobium.*

Observer	Sample	Property	Temperature, °C.				
			0	100	200	300	600
N.P.L.	<i>A</i>	Thermal conductivity *	(0.106)	0.112	0.118	0.124	...
		Electrical resistivity †	16.8 <sub>6</sub>	21.2	25.5	29.6	...
		Lorenz function ‡	(0.65 <sub>4</sub> )	0.63 <sub>6</sub>	0.63 <sub>6</sub>	0.64	...
	<i>B</i>	Thermal conductivity *	(0.115)	0.121	0.126	...	...
		Electrical resistivity †	(15.4)	(19.5)	(23.5)	...	...
		Lorenz function ‡	(0.64 <sub>9</sub> )	(0.63 <sub>2</sub> )	(0.62 <sub>6</sub> )	...	...
Tottle		Thermal conductivity *	0.125	0.130	0.135	0.140	0.156
		Electrical resistivity †	15.22	19.18	23.13	27.09	38.96
		Lorenz function ‡	0.697	0.668	0.660	0.662	0.696

\* Expressed in cal.cm./cm.<sup>2</sup> sec. °C.

† Expressed in microhm cm.<sup>2</sup>/cm.

‡ Expressed in 10° cal.ohm/sec. °C. °K.

Values in parentheses involve extrapolation.

apparatus which could be regarded as being of known thermal conductivity and would therefore serve as an independent check of the method used.

Mr. D. A. ROBINS,† B.Sc., A.I.M. (Member): I should like to comment on the results reported by Mr. Tottle for a series of niobium-oxygen alloys containing up to 0.565 wt.-% oxygen (Table V, p. 377). Seybolt‡ has shown that the solubility of oxygen in niobium is temperature-dependent and decreases from 1.0 wt.-% at 1100° C. to 0.25 wt.-% at 775° C. The amount of oxygen remaining in solution in a given alloy will, therefore, vary with the heat-treatment it has received and, since the effect on the mechanical properties of oxygen in solution will differ from the effect of a precipitated oxide phase, the properties of an alloy should be determined by the heat-treatment.

The alloys examined by Mr. Tottle were homogenized at 1400° C. after oxidation, but no information on the rate of cooling is given. The continuous increase in electrical resistivity with increasing oxygen content shown in Table V would suggest, however, that the cooling rate was sufficiently rapid to retain the oxygen in solution, and perhaps the author would confirm that this was, in fact, the case. It would also seem that the hardening effect of the gas in the alloys contain-

one of the alloys, as compared with 87 for the unalloyed metal, is inconsistent with their respective tensile properties. Similar anomalous results are quoted for the molybdenum and tungsten alloys, and one cannot ascertain what proportion of the changes in properties is due to impurities, defects, or to alloy content. With reference to Table V, I should like to ask Mr. Tottle how the oxygen contents were determined and whether the nitrogen contents are available, because wide differences in the relation between oxygen content and hardness are apparent in the results quoted and those determined by the N.P.L.\*\* and by Seybolt.‡ Thus, up to a hardness of about 150 V.P.N. the results of the three investigations agree, but wide divergences occur at higher hardness values. It is apparent that an accurate estimation of the gas content is an important consideration in assessing the mechanical properties of niobium and its alloys.

Dr. G. A. GEACH,†† M.Sc., F.I.M. (Member): Figures given by Mr. Tottle in Table III (p. 376) of his paper are valuable in showing how well niobium retains its strength up to 550° C. This retention of strength to yet higher temperatures is illustrated by values of hardness measured in the A.E.I. Research Laboratory (Table C). Comparison of the fall in hardness of niobium between 20° and 400° C. and 400° and

\* The work referred to formed part of the research programme of the National Physical Laboratory and is published by permission of the Director of the Laboratory. Mr. R. P. Tye assisted with the observations.

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‡ A. U. Seybolt, *Trans. Amer. Inst. Min. Met. Eng.*, 1954, 200, 774.

§ A. G. Knappton, *Nature*, 1955, 175, 730.

|| R. Kieffer, F. Benesovsky, and H. Schmid, *Z. Metallkunde*, 1956, 47, 247.

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\*\* T. H. Schofield, this vol., p. 373.

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800° C. with that of tungsten brings out strikingly the high-temperature strength of niobium. Values for zirconium, a material of possible importance in nuclear engineering, are also given in the table.

TABLE C.—Hardness at Various Temperatures in Terms of the Hardness of Each Metal at 220° C.

Metal	20° C.	400° C.	800° C.
Niobium . . .	1.0	0.7	0.5
Tungsten . . .	1.0	0.3	0.3
Zirconium . . .	1.0	0.6	0.15

As Dr. McIntosh says (p. 369), niobium has been thought to harden on working at a much lower rate than most metals. Results given by Mr. Williams in Fig. 6 (p. 391), showing appreciable work-hardening, are in surprising contradiction to this belief. It would therefore be helpful to know more of the experiment reported. Has Mr. Williams found work-hardening curves of this same form for niobium samples of any other purity? Measurements made in the A.E.I. Research Laboratory on one specimen suggest that rapid hardening of niobium occurs during the first small amount of deformation, but that little further change takes place between 4 and 96% reduction in thickness by rolling. Unlike the results given by Mr. Williams, these measurements show little work-hardening to occur over most of the working range of the metal.

Can Mr. Williams say what annealing treatment is necessary to soften the work-hardened niobium?

It would be interesting to know of any special methods of analysis used to determine oxygen or other impurities in the course of the work reported in these papers.

Mr. S. S. SMITH,\* M.Met., F.I.M. (Member): In order to ensure that niobium has a rosy commercial future, it will be necessary to seek some alternative to the elegant consolidation procedure described by Mr. Williams. Work-pieces vastly larger than  $18 \times 2\frac{1}{2} \times 1$  in. must be forthcoming, and the suitability of vacuum-melting as a means of consolidation has therefore been considered. It is not yet practicable to melt in quantity, and so evaluation buttons of the kind used effectively to control the processing of titanium and zirconium have been made. By reference to these, it should be possible to infer what would happen in the handling of greater bulk. It seems, in fact, that if commercial-purity powder is remelted, without prior sintering, the ingot hardness will be of the order of 450 V.P.N. On the other hand, material already at a hardness of 100–140 V.P.N. should not increase significantly in hardness after melting. Overall reductions in thickness of the order of 98% should then be achieved in the cold. Niobium is indeed a highly malleable metal. To make it commercially important, it will be necessary to provide softer material for melting and to improve scaling-resistance by suitable alloying.

Dr. F. G. Cox †: Whilst agreeing with the general remarks on welding of niobium made by Mr. Williams I should like to add a few points from our own experience.

We have found that with a reactive metal such as niobium the use of D.C. is strongly to be preferred. With A.C. an extensive, shallow molten pool is formed and the argon shield from an unmodified argon-arc torch is insufficient to protect the weld. Welding in a box completely filled with argon is therefore essential. However, with D.C., and the consequent deep restricted pool, argon protection as provided by the unmodified torch is sufficient to give a sound weld with

similar properties to the base metal, provided also that the back of the weld has been protected. Filler rod should be avoided, as the rod tends to oxidize outside the protection of the argon blanket, the oxide subsequently being dissolved in the weld metal. Wherever possible it is preferable to design the joint in such a way that no filler rod is required or, if this is not possible, to place the filler rod in the joint before welding. With metal 0.050 in. thick or more, or where a manipulated hand-fed filler rod is essential, it is necessary to use an argon-filled box.

A further advantage of using D.C. with a metal of such high melting point is that the heat is concentrated in the weld metal and tungsten contamination is minimized.

Dr. MCINTOSH (*in reply*): It is gratifying to find that so much interest has been stimulated in niobium, and the full account given by Dr. Argent shows that the work being initiated in Sheffield University promises to be of importance in furthering our knowledge of the metal and its alloys. The Research and Development Branch of the U.K.A.E.A. has undertaken to sponsor a considerable proportion of this effort, together with work in other centres, so that a fuller knowledge can be obtained.

We are aware that separation from tantalum is necessary only in specific instances, particularly where neutron-absorption cross-section is involved. The presence of tantalum does not affect the corrosion of niobium in acid aqueous media, and American results ‡ suggest that the oxidation rate in air is also little affected. American workers have also carried out a considerable number of sorting tests on the oxidation-resistance of niobium alloys and conclude that 25 at.-% titanium, 5 at.-% molybdenum, 10 at.-% vanadium, and 25 at.-% chromium represent the optimum binary additions for oxidation-resistance in the range 600°–1000° C.

The Sheffield results on aluminium alloys support our own findings on the working properties of niobium–20 at.-% aluminium alloys. These were successfully prepared by arc-melting, but hot rolling proved difficult. The material was brittle at room temperature. Further fundamental advances in the effect of alloying on the oxidation-resistance of niobium would appear to await a study of the electrical properties of the oxide film, and an assessment of how the covalent ionic forces are modified by the substitution of foreign atoms in the ionic lattice.

Dr. Goldschmidt provides welcome additional information on the niobium–iron system. It is pleasing to note that he also considers the atomic size factor of some value as an approach to niobium alloy selection, and that the results of his analysis agree in general with those quoted in the paper. This approach is, of course, limited by the tendency to compound formation with many elements. Some attention has already been given to the niobium–aluminium alloys. With the niobium–silicon material, a knowledge of the composition range in which the high-temperature oxidation-resistance was found, would be of value. The American results ‡ suggest no improvement with up to 5 at.-% silicon, an actual increase in oxidation rate at 1100° C. being recorded. Higher oxidation-resistance at 1200° than at 1000° C., as reported by Dr. Goldschmidt, may result from appreciable sintering effects at the higher temperature which tend to make the oxide film less pervious to gas.

The application of thermodynamics to the prediction of alloy diagrams, as described by Dr. van Lancker, is difficult because of the lack of suitable data. Moreover, the determination of the relevant properties with the necessary precision is in many cases more difficult than the determination of an actual equilibrium diagram.

In reply to Dr. Dennis, it is neither possible nor desirable

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‡ U.S. Atomic Energy Commission Publ., 1957, (BMI-1169).



to give a general answer to his queries, which fall within the field of reactor technology. The engineering characteristics of the circuit are of such predominating importance that it is unwise to rely on a theoretical appreciation which must be deficient because based on an oversimplified approach to a system which, after much experimental work, is recognized to be exceedingly complex.

In the U.K.A.E.A. it has been shown that it is only when all aspects are not considered that the corrosion effects of sodium containing oxygen present difficulty.

The formation of niobium carbide is possible, although such an effect has not yet been observed. Most experience has been obtained on circuits using stainless-steel components in which the carbide has been stabilized by niobium or titanium additions.

Dr. Powell refers to the 6% discrepancy between the values of the Lorenz function for niobium obtained at the N.P.L. and those reported by Mr. Tottle. Further determinations in the Culcheth laboratories recently confirm the values reported by Tottle over the temperature range of interest. The reported differences in thermal conductivity and Lorenz function probably arise from real differences in density, grain-size, and impurity content of the samples.

The rapid hardening of niobium with the first small amounts of plastic deformation, reported by Dr. Geach, has also been found with high-purity, electron-bombardment-melted niobium at Culcheth. When small amounts of gaseous impurities are present, however, the curve shown in Fig. 6 (p. 391) of Mr. Williams' paper is typical. The presence of impurities such as carbon, oxygen, and nitrogen in the material to which Fig. 6 applies is indicated by its high initial hardness, some 40 points above that of high-purity niobium. With this latter material, work-hardening, after the first small strain, is very small indeed over a wide range of reductions in thickness, as indicated by the following values:

Percentage Reduction in Thickness by Rolling	Hardness, V.P.N.	Percentage Reduction in Thickness by Rolling	Hardness, V.P.N.
0	47	54	79
15	75	64	70
24	78	74	80
34	74	84	74
44	71	100	80-100

The presence of small amounts of oxygen, carbon, and nitrogen produces other effects on the mechanical properties besides altering the work-hardening characteristics. A well-defined, discontinuous yield point is found at temperatures up to 400° C. in such impure material, and there is evidence of some strain-ageing and blue-brittleness effects.

Mr. SCHOFIELD (*in reply*): I wish to thank Dr. van Lancker for his interesting theoretical approach to the determination of solidus and liquidus curves. It would appear, however, that much of the data required for such determinations are not generally known with sufficient accuracy, even if it is assumed that the main premises for the calculations are valid. Moreover, the experimental errors involved in the determination of the melting points of highly reactive and high-melting-point metals are generally appreciable, and it would seem rather absurd to apply temperature corrections involving fractions of a degree Celsius.

Mr. TOTTE (*in reply*): As regards Dr. Powell's comments, the apparatus described for thermal-conductivity measurements was thoroughly tested, using conventional metals of high purity, before the work on niobium was undertaken. Many samples of niobium, from a variety of sources, were initially investigated, and the results quoted from the N.P.L. would suggest to us the presence of porosity. This seems a more likely explanation of the 5% difference in figures for thermal conductivity than the methods used, especially in view of our early experience with poorly sintered or worked material.

The alloys quoted by Mr. Robins were cooled from 1400° C. by removing the furnace and allowing the vacuum tube to cool in air, as practised by Seybolt. All the alloys were in the form of solid solutions after this treatment, except the one containing 0.565 wt.-% oxygen, in which a precipitate was detected by microscopic examination.

No slow cooling was carried out, but alloys containing 0.315-0.565 wt.-% oxygen were aged for 72 hr. at 800° C. The hardness was reduced by this means to the order of 250-260 V.P.N. for all the alloys. A precipitate was detected in those with 0.41 and 0.565 wt.-% oxygen, as a result of the ageing treatment.

In reply to Mr. Schofield, we believe that the results quoted in our paper agree reasonably well with those of Seybolt up to 250 V.P.N., but above this level only one value of those obtained by Seybolt can be used in comparison. We do not consider that the higher values can be compared, as a fast rate of cooling was not employed. The effect of impurities and defects is indeed quite startling in the alloys, and this point was made in the paper, indicating that the alloying metals obtainable were not prepared with the same degree of control as the niobium which we ourselves made! Oxygen contents were determined by vacuum fusion and gas analysis, with an accuracy of approximately 10% at 0.1 wt.-%. Nitrogen was present at such a low level that the accuracy cannot be estimated, but it did not exceed 0.006 wt.-% in the alloys. We believe that the disposition of even minute traces of particular impurities, influenced by subsequent fabrication and heat-treatment, may be the cause of the variations in properties observed.

Dr. MILLER (*in reply*): Until a few years ago niobium was in short supply and the use of the metal was discouraged, at least for Service projects; this also tended to discourage research into its properties. By 1953 or shortly thereafter, large deposits of the ore were found in Africa and later further extensive discoveries were made in Canada. These discoveries completely changed the status of niobium, and interest in it increased rapidly, particularly as it displayed good high-temperature properties. In the short time that research has been in progress, it has been shown that niobium alloys possess high-temperature properties as good as those of molybdenum, but unfortunately niobium, like molybdenum, is not resistant to oxidation. However, it behaves much better than molybdenum, the oxidation of which has been described as "catastrophic".

Alloys of niobium have been produced which are many times better than molybdenum, though they still fall short of what is required for a material operating for long periods at temperatures above 1000° C. Work is continuing in an attempt to produce alloys which will be satisfactory at these temperatures. An alternative approach is to protect the niobium alloy by means of a coating, as in the case of molybdenum. If this could be done to niobium alloys, then the product would be better than in the case of molybdenum, because if the coating should fail there would be an added margin of safety.

There are two main interests in niobium; for nuclear-energy purposes and as a high-temperature material. In the case of the nuclear application there is a further sub-division. In the United Kingdom niobium is considered to be a canning material; in fact, it is the metal which has been used as a canning material for the Dounreay fast reactor. In the U.S.A., the principal interest in niobium for nuclear purposes appears to be in alloys of uranium containing niobium. These alloys are much more resistant than uranium to attack by hot water and, even although a protective canning material would still be used with fuel elements, there is an increased factor of safety in the knowledge that if the canning should fail the uranium-niobium alloy would not be rapidly attacked, as is the case with the unalloyed metal. It is very probable that the niobium required for the two projects, i.e. nuclear



energy and the aircraft industry, will be of two different types. In the first case one visualizes a very pure and expensive metal. For use at high temperatures, it will be necessary to employ cheaper material; the way to obtain a cheaper material is to produce one that is less pure, and attempts will be made to reduce the cost of processing, probably by not removing the metals associated with niobium in the ores and which are expensive to separate. This assumes that metals such as tantalum and titanium, present in the ore, do not diminish the oxidation-resistant properties of the alloys.

Dr. Argent has suggested that a large-scale demand for ferro-niobium might lead to a reduction in the cost of niobium. This is true to some extent, although it cannot affect the cost of the extraction, which is the main expense. Without a general development in the usage of niobium, it is difficult to see where the niobium ores will come from, as the quantities of pure niobium required are going to be quite small and probably will not exceed 50 tons a year for both the U.S.A. and the U.K. This is not the consumption at present but an estimated requirement for the future.

Dr. Dennis enquired what were the relative positions of development of niobium in the U.S.A. and the U.K. Niobium was produced in the U.S.A. at least twenty years ago, but the material was available only in small quantities, and it was not particularly satisfactory, as it contained appreciable amounts of carbon and oxygen. This material was quite unsuitable for the purpose proposed by the U.K.A.E.A., and it was necessary to develop the production of a much purer metal, capable of being consolidated and formed into the components required by the Authority. In the meantime, the material produced in the U.S.A. has considerably improved.

Dr. Edeleanu wonders whether it would be worth reconsidering the possibility of producing massive niobium by electrochemical means. This presumably means producing solid cathodes of niobium. If this is so, then I have no knowledge of anyone ever attempting to do this either with niobium or similar metals. If Dr. Edeleanu means the production of a coarse niobium powder by electrolysis, some work was carried out a long time ago by the Fansteel Metallurgical Corporation, but they abandoned it in favour of the oxide/carbide reduction because they obtained such poor efficiencies. In general, powder produced by electrolysis, at least of the reactive metals such as zirconium, titanium, and tantalum, contains considerable amounts of oxygen. In the case of titanium and zirconium, one of the problems has been to produce a coarse powder without oxidation. In the case of the electrorefining of titanium and zirconium, this problem has been overcome and extremely pure metal has been obtained, but a great deal of trouble is still encountered in the electrolysis of titanium from salt baths.

Dr. Edeleanu asks whether it must all end up as powder. This depends on the temperature employed during the reduction of metal, and the use of processes involving temperatures above the melting point of niobium would introduce more problems than have to be faced in converting niobium powder to metal.

Mr. O'DRISCOLL (*in reply*): I agree that the figure of approximately 107 k.cal. given by Dr. Kubaschewski for the free energy of dissociation of  $2\text{NbO}$  at  $2000^\circ\text{C}$ . is correct. The value given in our paper was in error owing to the inaccuracy of the data on which the calculations were based.

Mr. WILLIAMS (*in reply*): The cost of niobium has been frequently referred to, particularly in relation to the comparatively high levels of impurity present in the raw niobium powder.

The price of niobium metal is best considered in relation to the ductile product, as this includes the costs incurred as a result of using impure starting material. The major items are:

- (1) Raw material, usually ferro-niobium in the U.K.
- (2) Chemical purification and reduction to pure metal.
- (3) Sintering.

The price of ferro-niobium represents only a small fraction (less than 5%) of the cost of the ductile metal. Any decrease in the price of the ferro-alloy would thus result in only a marginal decrease in the cost of the finished product. The reduction in price of the raw-metal powder which would result from operating the chemical purification and reduction plant on a much larger scale than at present, would in all probability be far greater than any decrease due to minor changes in the price of the ferro-alloy.

All the production methods hitherto proposed, including the chloride, fluoride, and oxide processes, yield the metal in powder form. The chloride route would at first sight seem to be potentially the most attractive, as the metal can be produced to very low oxygen and carbon specifications. However, recent developments suggest that the fluoride route can be operated to give equally good material; in addition, recent improvements in the sintering process, particularly associated with increasing the scale of operation, have considerably reduced the price penalty imposed for removing carbon and oxygen to the levels at present considered desirable.

One of the key issues, which has been referred to by Mr. S. S. Smith, is associated with arc-melting as a technique for consolidation. It is now generally recognized that but little purification from carbon and oxygen can be expected during this operation, but two possibilities can be considered where the process might be acceptable. First, the production of metal powder of a much higher purity than that produced at present, and secondly, acceptance of a higher level of impurities in the finished metal. The adoption of the process would certainly make the metal available in masses of greater cross-sectional area than can be contemplated at present, but it would, of course, also necessitate the development of methods for fabricating the large ingots obtained. Recent advances in fabricating titanium and zirconium, using this route, suggest that we have already gone a long way towards solving the problems likely to arise with niobium.

All these factors, including method of reduction, purity of powder, and method of conversion to massive metal, are closely interrelated, and the final selection of an overall process must be based on economics. Development work is proceeding at a number of laboratories in Britain, but clearly no firm decision as to the ultimate choice of process is possible at present.

Dr. Geach refers to the work-hardening curve on p. 391 of my paper. This is based on the examination of standard-grade niobium processed as described in the text, the chemical composition in this particular instance including 0.02 wt.-% oxygen and 0.01 wt.-% carbon. Tests on metals of a small range of compositions show that increasing the oxygen content to 0.13 wt.-% gives a curve of similar shape, in which the individual hardness values are increased by approximately 50 V.P.N. Preliminary tests suggest that small variations in carbon content change the shape of the curve, the initial portion being rather steeper, thus approaching more closely the results quoted by Dr. Geach. In no case have we noted the very marked increase in hardness reported by Dr. Geach to occur during the first 4% of cold working. A full examination of the effect of individual impurity elements on the hardness of niobium, including a study of the interaction of one impurity element with another, would provide a very interesting field of study, which as far as I am aware has not been covered for this metal.

Material of a much higher order of purity has recently been produced at the Culcheth Laboratories, using electron-bombardment techniques, and this exhibits the very low rate of work-hardening referred to by Dr. McIntosh.

The annealing of cold-worked niobium is normally carried out in a vacuum better than  $1 \times 10^{-4}$  mm. at a temperature



of 1200° C. The metal is not particularly susceptible to rapid grain growth, and annealing times up to 30 min., depending upon the thickness of the sheet, have been found satisfactory. The leak-rate of the apparatus must necessarily be kept as low as possible.

Dr. Edeleanu raises a very interesting speculation as to whether we must always start from niobium powder. The individual problems of reduction and consolidation are difficult, but rapid progress is being made both in the production of powder of higher purity and in improving the sintering techniques. The economic advantage associated with the

development of a process to give the pure massive metal in one step is problematical for the rates of output envisaged during the next few years.

Whilst I agree in general with Dr. Cox's remark that direct current is preferable for welding, experience suggests that, assuming the correct conditions are selected for either A.C. or D.C., then the difference in weld-pool configuration is not so great that the considerable differences attributed to argon coverage from a standard torch would be expected. We have found it necessary to modify the gas shield and to use an argon "backing" to achieve satisfactory results.

## Discussion

### Magnesium-Lithium Alloys \*

Dr. W. HUME-ROTHERY, † O.B.E., F.R.S. (Member): The idea of using magnesium-lithium-base alloys for practical purposes arose independently in Great Britain and the U.S.A. nearly 20 years ago. The constitution of some of the alloys was discussed in 1946, ‡ when a prominent metallurgist expressed the view that "the alloys can scarcely be considered even the germ of a practical development proposition". Experimental work on both the constitution and mechanical properties of these alloys has, however continued, and great credit is due to Professor Jones and his colleagues at Cardiff for the way in which they have overcome the experimental difficulties. Their work, and also that of Messrs. J. Stone and Co., Ltd., has shown that these alloys are at least a practical possibility, and the position at the moment is very tantalizing, since a very small increase in the structural stability of the alloys might make them of real value.

The outstanding feature of the Cardiff work is the marked effect of silver. It is possible that the suggested relation to a valency effect is really the result of more than one factor. This view is confirmed by the fact that the so-called "effective valencies" give a better correlation, because the effective valencies appear really to be lattice-spacing numbers, rather than valencies in the ordinary sense. In passing along the sequence  $\text{Ag} \rightarrow \text{Cd} \rightarrow \text{In} \rightarrow \text{Sn} \rightarrow \text{Sb}$ , there is increasing valency and increasing electronegative character of the element; there is also a rapid shrinking of the electron cloud of the  $(4d)^{10}$  sub-group of the underlying ion. It is perhaps significant that, of the elements dealt with, silver has much the largest ion, and it may be this which impedes its movement and so increases its stabilizing power.

It would be helpful if Professor Jones and Dr. Hogg would explain in greater detail what is meant by saying that ternary alloys have the f.c.c. NaTl structure. In the binary NaTl structure, each atom is at the centre of a cube, with four like and four unlike atoms at the corners, and from some points of view the structure may be considered as a superlattice of a body-centred cube, although the larger unit cell (8 small cubes) is properly called face-centred cubic. With a composition  $\text{MgLi}_2\text{Zn}$  different arrangements are possible, and some of these might be distinguished by the presence or absence of the (200) reflection of the larger unit.

According to the authors, the alloys become unstable as soon as the  $\text{MgLi}_2\text{Zn}$  phase appears. If it is regarded as a superlattice, the ordered structure would be favoured by increasing electrochemical factor, in agreement with the observed effects of tin and antimony. This might also agree with the effect of nickel if the latter absorbed electrons into its  $d$  shell.

Mr. R. CHADWICK, § M.A., F.I.M. (Member): The following remarks concerning the papers by Professor Jones and his collaborator are supplemented by some hitherto unpublished data on the mechanical properties and age-hardening characteristics of binary and more complex alloys of magnesium and lithium. These are from work carried out in the Research Laboratories of Imperial Chemical Industries, Ltd., Metals Division, in collaboration with Mr. K. G. Sumner.

Professor Jones concerns himself mainly with the  $\beta$ -phase alloys which have a body-centred cubic structure. Because of the more readily available modes of deformation these alloys are much more amenable to cold working than  $\alpha$ -phase hexagonal alloys, although Professor Jones shows that alloys in the  $\alpha/\beta$  range are quite readily cold worked. It does not seem to have been fully appreciated hitherto that lithium greatly improves cold-working properties within the  $\alpha$ -range of alloys. Thus, under the particular conditions of experiment which we employed, annealed strip of pure magnesium was capable of only 15% reduction in thickness by cold rolling without cracking, while an alloy containing 3% lithium, although entirely free from  $\beta$  constituent, could sustain reductions in thickness of up to 60%. The fact that this greater amenability to cold work can be brought about within the  $\alpha$  range would seem to have considerable theoretical significance, quite apart from its practical value in relation to working properties.

The usefulness of these quite small amounts of lithium in improving the cold-working properties is not confined to binary alloys. In view of the high cost of lithium and the difficulties in melting and casting alloys of high lithium content, it would be desirable to investigate lower ranges of lithium content in the more complex alloy systems, and to reduce alloy contents more generally. There is very often a tendency, in carrying out early exploratory research on new alloy systems, to attempt to attain the highest possible mechanical properties without regard to the many difficulties encountered by the use of very high alloy contents. When it comes to commercial fabrication of the materials, the ability to cast and work readily on normal metallurgical plant, and to achieve a satisfactory rate of output, must be taken into account. It is in this direction that magnesium alloys have hitherto suffered seriously, the cost of conversion into wrought forms being such as to render the products wholly unattractive. A serious plea is therefore made for studies of milder alloys, which might be cast with less difficulty and more readily cold worked.

Some data on ternary magnesium-aluminium-lithium alloys in a relatively low range of lithium and aluminium

\* Joint discussion on the following papers published in the *Journal*: W. R. D. Jones (1955-56, 84, 364); M. W. Toaz and E. J. Ripling (this vol., p. 137); W. R. D. Jones and G. V. Hogg (this vol., p. 255).

† George Kelley Reader in Metallurgy, University of Oxford.

‡ *J. Inst. Metals*, 1946, 72, 538 (discussion).

§ Manager, Technical Department, Imperial Chemical Industries, Ltd., Metals Division, Birmingham.



contents are illustrated in Figs A-D. These show contours of ultimate tensile strength and elongation for sheet material, as quenched from 300° C., and as fully softened by slow cooling, while Fig. E indicates maximum possible cold-rolling reductions without cracking in annealed sheet. It will be seen that from the strength point of view the optimum lithium content is about 3%, while up to 5% or so of lithium is rather more desirable from the point of view of ductility. With more than about 3% aluminium, ductility

unlikely that these properties would have been sustained at intermediate temperatures of, say, 30° C., which is well within the range which might be expected under normal commercial storage. The attempts at stabilization must therefore be regarded as a failure. We carried out some work on the effect of cerium and silver as stabilizers for magnesium-aluminium-lithium and magnesium-aluminium-zinc-lithium alloys, some of the results of which are shown in Table A. The amounts of cerium and lithium added were

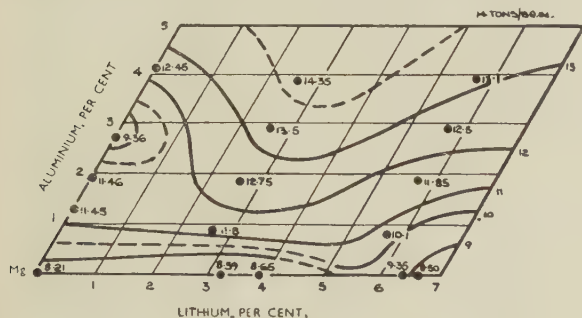


FIG. A.—U.T.S. as quenched from 300° C.

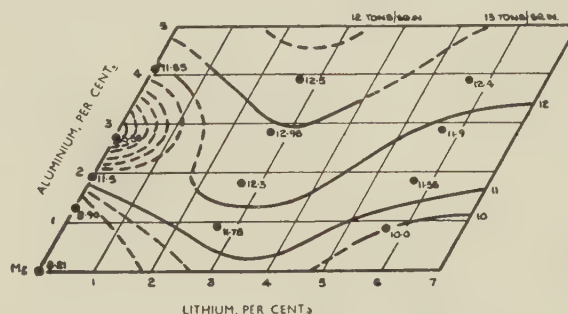


FIG. B.—U.T.S. as slowly cooled.

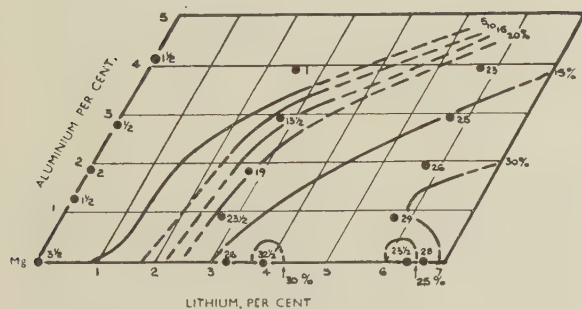


FIG. C.—Elongation as quenched from 300° C.

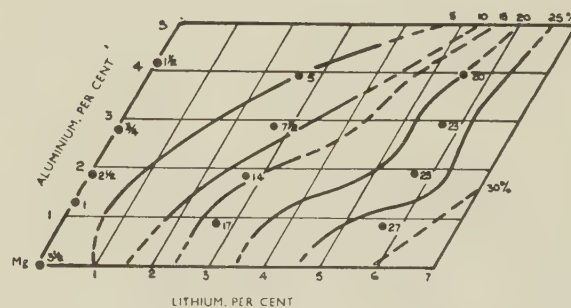


FIG. D.—Elongation as slowly cooled.

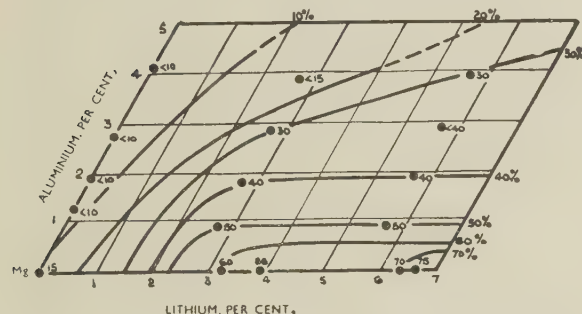


FIG. E.—Maximum Possible Cold-Rolling Reduction of Magnesium-Aluminium-Lithium Alloy Sheet.

falls to a value which renders the material unsuitable for commercial applications. The optimum alloy thus contains about 4% lithium and 2-3% aluminium, and has a tensile strength of 12-13 tons/in.<sup>2</sup>, while cold-working properties may be regarded as adequate. At 3% lithium content the  $\alpha$ -phase extends only to about 0.5% aluminium, so that these alloys have a duplex structure.

We were also interested to learn of Professor Jones's attempts to stabilize the heat-treatable alloys by the addition of various elements, including cerium and silver. All the alloys softened fairly rapidly at 50° C., although high-strength values in a number of alloys were held at 16° C. It seems

smaller than those used by Professor Jones, but they produced appreciable enhancement of ductility and cold-working properties, and cerium had a pronounced beneficial effect on age-hardening properties of certain alloys. In the heat-treated condition all the alloys softened progressively in the range 30°-50° C., the properties corresponding eventually to those obtained in the slowly cooled condition. It is thus evident that the highest useful tensile-strength values are in the range 12-14 tons/in.<sup>2</sup>. The alloys described all contained an addition of 0.1-0.2% manganese, to neutralize the ill effects of contamination by traces of sodium.

From our own fairly extensive investigations of lithium

bearing alloys, mainly within the magnesium-aluminium-zinc-lithium system, with minor additions, the conclusion reached was that very little possibility exists of achieving stability and, in fact, none of the work provided any encouragement for the belief that softening temperatures could be raised sufficiently to enable the age-hardened condition to be retained even for the range of ambient temperature in normal room-temperature use. If this is accepted, then the small gain in strength could not possibly justify the use of high percentages of lithium under present conditions. Smaller amounts in the range 3-5% have a worth-while effect in increasing amenability to cold working, and with some reduction in the price of lithium, such an addition might well

by the magnesium, the  $MgCl_2$  formed would still have removed the sodium. Similarly with the zirconium. This was added as a master alloy containing about 2%  $MgCl_2$ .

The chemical background to the sodium-contamination difficulties with magnesium-lithium alloys is perhaps of some interest. The stability of  $LiCl$  is much greater than that of  $MgCl_2$  and of the same order as those of  $NaCl$ ,  $KCl$ ,  $CaCl_2$ , and  $BaCl_2$ . In consequence, none of these salts can be safely used as a basis for fluxes for magnesium-lithium alloys, and even the most stable,  $BaCl_2$ , is appreciably reduced by lithium. Sodium tends to form grain-boundary films of low contact angle in magnesium and in consequence can be disastrous to the mechanical properties of castings. In the other

TABLE A.—Mechanical Properties of Magnesium Alloy Sheet.

Composition, % (remainder magnesium)					U.T.S., tons/in.*			Max. Possible Rolling Reduction, %
Aluminium	Lithium	Zinc	Cerium *	Silver	Slowly Cooled from 300° C.	Quenched from 300° C.	Room-Tem- perature Aged	
6	10	5	...	...	12.2	18.8	19.6	72
		8	0.5	...	10.7	19.4	25.0	>90
10	10	1	...	...	12.4	18.0	20.1	85
		1	0.5	...	11.5	16.2	19.0	>90
		1	...	1.0	13.2	17.4	17.3	>85
10	12	...	...	...	9.3	17.6	21.8	90
		...	0.5	...	9.5	16.2	22.1	>90
		...	...	1.0	10.9	17.9	23.8	>85
		...	...	...	...	...	...	...

\* Total rare-earth-metal content.

be commercially justifiable. An alloy based on the well-tried magnesium-2% manganese, with from 2 to 3% lithium, is one which particularly commends itself,\* providing a tensile strength of about 12 tons/in.<sup>2</sup>, with good cold-working properties. This range of lithium contents also confers maximum resistance to corrosion.

Dr. E. F. EMLEY,† B.Sc., F.I.M., F.R.I.C (Member): It has been known since about 1950 ‡ that for full ductility in the higher-strength magnesium-lithium alloys the sodium content should be kept below about 0.01%. All three alloys studied by Mr. Toaz and Dr. Ripling contain more than this amount of sodium and, as the authors point out, the sodium contents of their samples increase with increasing lithium content. One would like to know at the outset whether or not the interesting phenomena they describe are associated with sodium or inherent in the magnesium-lithium alloys, and it is to be hoped that the authors will make some check tests on the flow and fracture characteristics of alloys with satisfactorily low sodium contents, particularly the cubic alloy, in order to settle this point.

Professor Jones has stated that the presence of manganese or zirconium enables more sodium to be tolerated in the magnesium-lithium alloys than would otherwise be the case. It seems to me that this is likely to be due to partial removal of sodium during the alloying of these elements. Manganese was added to the magnesium-lithium alloy as  $MnCl_2$ , and this salt should be reduced by the lithium rather than by the magnesium. The  $LiCl$  liberated would then flux out the bulk of the sodium. If some of the  $MnCl_2$  had been reduced

magnesium alloys, no difficulties arise in practice, since any  $NaCl$  in the fluxes used is not appreciably reduced by magnesium, particularly in view of the  $MgCl_2$  normally present in the fluxes. With the magnesium-lithium alloys, however, the lithium will partially reduce small amounts of  $NaCl$  present in the  $LiCl$ - $LiF$  flux used.

Actually,  $LiCl$  is slightly more stable than  $NaCl$  at operating temperatures (1000° K.), so it would seem impossible to flux out sodium without removing lithium preferentially. Fortunately, however, sodium shows a large immiscibility gap with magnesium, whereas lithium forms a compound, and the net effect is to make  $NaCl$  less reducible by magnesium than is  $LiCl$ . Thus, in the chemical displacement series for chlorides with respect to magnesium, lithium is slightly more noble than sodium, but in the electropotential series for chlorides as shown on an Ellingham diagram,§ the reverse is the case.

Professor Jones's results are unlikely to be affected by sodium contamination, since he has used high-purity lithium and melted under argon. As some melts were made with  $LiCl$ - $LiF$  flux, I think it would be desirable to have on record the approximate sodium contents of the lithium halides used, if this information is available.

From Professor Jones's work, it appears that relatively little zirconium can dissolve in magnesium containing lithium. This is in accordance with the results of some experiments we made with the  $\alpha$  alloys, in which we managed to incorporate only 0.3-0.4% zirconium solubly. In addition to the method used by Jones involving a magnesium-zirconium master alloy,|| we also tried adding high-purity lithium, either molten or as pre-warmed lumps,¶ to magnesium-

\* British Patent No. 715,786.

† Chief Metallurgist, Magnesium Elektron, Ltd., Clifton Junction, near Manchester.

‡ P. D. Frost, J. H. Jackson, A. C. Loonam, and C. H. Lorig, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, 188, 1171.

R. J. M. Payne and J. D. L. Eynon, *ibid.*, 1951, 191, 557.

§ A diagram showing plots of the free energies of formation of

various metal chlorides as functions of temperature.

|| The salt content of this alloy (p. 376, Vol. 84) should read: 50%  $MgCl_2$  and 50%  $BaCl_2$ - $KCl$  eutectic.

¶ The lumps were quickly dipped in molten  $LiCl$  in order to preheat them and burn off the protective paraffin layer before adding to the melt.



zirconium alloy melts made by reducing a large excess of  $\text{Li}_2\text{ZrF}_6$ -LiCl salt mixture with magnesium. The grain refinement obtained was commensurate with the analysed soluble zirconium contents.

One could perhaps hardly expect zirconium, which is hexagonal, to nucleate the cubic alloys, but it would be interesting to see how much zirconium could be dissolved in these alloys and what effect if any it would have on the grain-size. Fig. 7 of Jones's paper (Plate LXIII, Vol. 84) shows a mixed cubic-hexagonal alloy. Perhaps Professor Jones could confirm that the 0.3% zirconium mentioned is an acid-soluble zirconium content determined in the conventional manner. Even so, the true dissolved zirconium content will be considerably less than the analysed figure in view of the very high content of insoluble zirconium-rich particles present (Fig. 7). These are probably the nitride,  $\text{ZrN}$ , and Professor Jones will recall that we confirmed this on a specimen of very similar microscopic appearance, provided by one of his colleagues, by extracting the particles chemically and examining their X-ray diffraction patterns.

As regards the practical possibility of stabilizing the properties of the magnesium-lithium alloys to give commercially useful materials, the prospects now appear remote. Jones and Hogg's work and that of Rowland, Armantrout, and Walsh\* leave little hope of finding a stabilizing element, and I believe similar conclusions were reached during work done by Mr. R. J. M. Payne of J. Stone and Co., Ltd. Mr. Payne's work has shown that the alloys possess the additional disadvantage of creeping badly at room temperatures under relatively low stress, and that this disadvantage applies also to ( $\alpha + \beta$ ) alloys. One suggestion for achieving stable tensile properties in the strong cubic alloys is to induce complete conversion of the unstable precipitate to the stable form ( $\text{MgLiX}$ ) before working. It may well be that the work-hardening capacity would be insufficient to permit the development of interesting properties; perhaps Professor Jones would care to comment on this point. The creep difficulties might be overcome by the use of the methods of powder metallurgy, but probably not without spoiling the outstanding ductility of the alloys.

There remains the possibility of improving the ductility of existing magnesium alloys, and in particular their ability to be cold worked, by additions of a few per cent. of lithium, as illustrated by Mr. Chadwick's results. Loonam† has pointed out that the axial ratio of the magnesium lattice is reduced by lithium and that at saturation it is very similar to that of titanium. It seems a great pity therefore that lithium is not fully compatible with zirconium in magnesium alloys.

Mr. R. J. M. PAYNE,‡ B.Sc., F.I.M. (Member): The following observations are based on work carried out by Mr. J. D. L. Eynon and myself at the works of J. Stone and Co. (Charlton), Ltd.

A valuable feature of Professor Jones's paper is the data on the properties of alloys in the cast state. It is the first time that such data have been published, as all the American work was carried out on wrought materials. We have noted the properties of the binary alloy, particularly its ductility, and have also noted that in several alloys containing aluminium, zinc, and cadmium the properties are very good indeed. This finding is fully confirmed by our own work. Most of our ternary alloys had somewhat higher lithium contents than those of Professor Jones, and the properties are even better than he reported. In order that the excellent properties obtainable in magnesium-lithium alloys in the

cast state may be recognized, the following examples are quoted:

	Proof Stress, tons/in. <sup>2</sup>	U.T.S., tons/in. <sup>2</sup>	Elongation, %
Mg-13½% Li-2% Al-1.5% Mn .	17.4	19.65	2
Mg-13½% Li-7½% Zn-1.5% Mn .	17.5	20.0	2

To us, these properties are impressive for material in the cast condition, not heat-treated, and having a density around 1.5 g./c.c.

The tensile properties quoted by Professor Jones for his wrought alloys, which are in many instances little better than those of his cast alloys, are much the same as those recorded by the American workers (the author does not claim otherwise) and here again our results agree with those reported. We also failed in a large number of cases, as did Professor Jones, to improve by heat-treatment the tensile properties of many cast or wrought alloys.

We have looked with a highly critical eye at the results presented in Professor Jones's two papers for indications of interference by sodium, but have found none: the only results that are at all surprising are those for the  $\beta$  alloys, whose elongation values even after annealing do not always match the 60% quoted for his cast 12% lithium alloy (Table I, Vol. 84, p. 365), or with our results:  $\beta$  alloys of this type, as prepared by us, invariably show 40% elongation in the cast state and 50% or more in the form of forged rod. Perhaps Professor Jones could offer some explanation for this discrepancy?

In the second paper Professor Jones and Dr. Hogg have confined themselves to wrought alloys and have studied the effect of a range of elements on stability, concealing the precise compositions of the alloys with which they worked from all but the most diligent by a most artful combination of weight percentages, atomic percentages, and magnesium:lithium ratios. There are obvious difficulties in defining "stability", and an arbitrary definition based on the time in which a given proportional loss of hardness occurs has been used. According to this definition, silver and copper emerge from the present work as good stabilizers, although the propriety of labelling as "stable" alloys such as those containing silver, which at room temperatures hardened progressively over the first month or two in a six-months' period, can be questioned: at least they did not over-age. Apart from these difficulties, the present work has confirmed the American (and our own) finding that silver is a useful addition in this connection. From the curves given it would appear that the influence of silver is to slow down the whole ageing process. It is interesting and somewhat surprising to learn that copper should have a similar influence, as it had earlier been believed that only elements having some fair solubility in the  $\beta$  phase were useful in this way.

Professor Jones and Dr. Hogg have attempted to correlate stability, as defined by them, with the valency of the added elements and hence with the electron:atom ratio. I am not proposing to discuss this aspect of the paper, but would briefly make two points. (i) The authors have arrived at their conclusion without taking into account two metals—indium and thallium—which American workers have reported to be beneficial to stability, or a third metal—manganese—which we have found useful in this same connection. It would be interesting to know how these elements, which are not univalent, fit into the picture, and I would ask whether the authors can add anything to the data given in Table 1 (p. 257). (ii) There seems to be some doubt as to whether one of the points that the authors rely upon to bear out their theory, i.e., that the stability of alloys increases with an

\* J. A. Rowland, C. E. Armantrout, and D. F. Walsh, *U.S. Bur. Mines Rep. Invest.*, 1956, (5250).

† A. C. Loonam, *Trans. Amer. Inst. Min. Met. Eng.*, 1949, 185,

867 (discussion).

‡ Chief Research Metallurgist, J. Stone and Co. (Charlton), Ltd., London.

increasing lithium content, is really true. Once again a definition of stability is involved, but if I understand matters aright, Dr. P. D. Frost, in discussing a paper by Busk, Leman, and Casey,\* virtually retracted the early conclusion that lithium improves stability, at least long-term stability. In point of fact much of the later American work was concerned with ( $\alpha + \beta$ ) alloys, for the reason that these were found to be more stable.

It seems that the present authors have arrived at just the same point as the Americans and, incidentally, ourselves, in confirming the good properties obtainable but finding no solution to over-ageing at temperatures encountered in ordinary conditions of service. This loss of properties on ageing is, however, by no means the only major problem these alloys present. A good appraisal was made by Dr. Leman

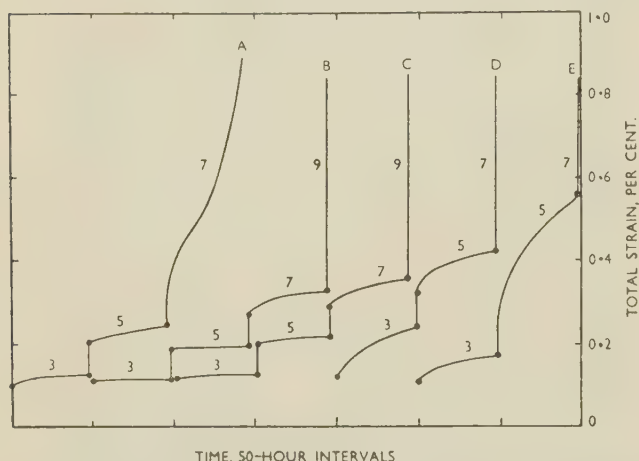


FIG. F.—Creep Curves for  $\beta$  and ( $\alpha + \beta$ ) Magnesium-Lithium Alloys in the Cast State at 50° C. The figures on the curves represent the load in tons/in.<sup>2</sup>.

	KEY				
	A	B	C*	D	E
Li, %	13.5	13.5	13.5	13.5	8.75
Al, %	2	2	2	...	7
Mn, %	...	1.5	...	1.5	...
Ag, %	...	...	5	...	...
Zn, %	...	...	...	7.5	...
Sn, %	...	...	...	...	1
0.1% P.S., tons/in. <sup>2</sup>	14.0	17.4	13.9	17.5	10.7
U.T.S., tons/in. <sup>2</sup>	18.0	19.6	13.9	20.0	16.1
Elongation, %	3	2	Nil	2	6

\* Heat-treated alloy.

of the Dow Chemical Co., in the discussion of a paper by Frost, Kura, and Eastwood.† Our own results confirmed the findings of the Dow workers in full, particularly with regard to the brittleness of alloys at high strength levels; to make the general outlook even blacker, however, our work indicated a further and major disqualification by showing that the alloys as a class have a very poor resistance to creep. Now it is possible that this poor resistance to creep and the tendency to overage have a common origin, but it is a short-coming of which I believe the American investigators were unaware and it is not referred to in the present papers. Just how poor the alloys are in creep at a temperature of only 50° C. is illustrated in Fig. F. This shows curves for alloys of five compositions in the cast state, the first four being of the all- $\beta$  type. The tests were of an exploratory nature only and were made by step-loading. The first shows a  $\beta$  alloy containing 2% aluminium creeping appreciably at 5 tons/in.<sup>2</sup> and extending rapidly at 7 tons/in.<sup>2</sup>. Now 5 tons/in.<sup>2</sup> represents only about one-third of the 0.1% proof stress at ordinary temperatures. The second curve, which shows

some improvement in creep properties, relates to the same alloy with a manganese addition, and the third to one containing silver. This latter alloy was so brittle as cast that it could not be machined into a test specimen and had to be "let down" by heat-treatment before testing. In both cases the alloys are creeping badly at stresses of less than half their proof stress. The fourth curve relates to a strong  $\beta$  alloy containing zinc and manganese; this is extending rapidly at only 3 tons/in.<sup>2</sup>, though its proof stress was 17½ tons/in.<sup>2</sup>.

After finding poor stability in  $\beta$  alloys, the American workers turned to alloys of lower lithium content, i.e. to ( $\alpha + \beta$ ) alloys, and found compositions in which the deterioration of tensile properties and loss of hardness due to over-ageing at moderate temperatures (50° and 100° C.) was small. The fifth curve in Fig. F relates to such an alloy, but it will be seen that the creep properties are even worse than those of  $\beta$  alloys.

Finally, in regard to the papers by Professor Jones, I would remark that up to now the various people who have worked with these alloys have, like ourselves, confined themselves to materials prepared by conventional melting and casting techniques. It now seems unlikely that a solution to creep and instability problems will be found so long as these techniques are adhered to, and a new approach, based on powder metallurgy or the co-extrusion of metal powders, which allows of the admixture of otherwise incompatible elements, would seem to be a more profitable line to follow.

The point that interests me in the paper by Mr. Toaz and Dr. Ripling is the indication of a brittle range in the magnesium-lithium alloys, particularly in the single-phase  $\beta$  alloy.

The authors suspect that sodium may have influenced their results, and a glance at the elongation values for as-received 11% lithium alloy tested at room temperature (shown as less than 20% in Fig. 15, p. 143), together with the analysis which gives a sodium content of 0.068%, establishes immediately that the material is unrepresentative of properly prepared magnesium-lithium alloys: room-temperature elongation values for cast  $\beta$  alloys containing about 11% lithium and of low sodium content, prepared by us, are invariably around 40% and for wrought alloy 50% or more. The results presented by Mr. Toaz and Dr. Ripling should therefore be regarded as relating only to the particular magnesium-lithium-sodium alloys used. Even though unrepresentative, they are nevertheless still of interest, and our knowledge of the effects of sodium has led me to wonder whether a brittle range would have been found at all if the alloys had been prepared from pure materials.

Having some  $\beta$  alloy available in the form of ½-in.-dia. forged bar, we thought it worth while to carry out one or two

TABLE B.—Tensile Properties of Magnesium-13% Lithium Alloy Bar.

Test Temp.	U.T.S., tons/in. <sup>2</sup>	Elongation, %	Reduction of Area, %
Room temp.	6.95	69	84
0° C.	8.4	50	78
-50° C.	10.22	30	64
-100° C.	9.94	33	70

tests at the same slow rate of straining as that used by the authors (0.05 in./min.) and temperatures around those at which brittle behaviour had been observed. The material available was actually a 13% lithium alloy, but within the  $\beta$ -phase field properties change only slowly with changing lithium content, and it is legitimate to compare the results given in Table B with those for the 11% alloy used by the

\* *Trans. Amer. Inst. Min. Met. Eng.*, 1951, 191, 556 (discussion).

† *ibid.*, p. 560 (discussion).



authors. Test specimens 0.427 in. in dia.  $\times$  1.5 in. gauge-length (approximately  $\sqrt[3]{A}$ ).

The results reported above may be compared with those in Fig. 5 (p. 139) and in Fig. 15. It will be seen that our elongation values are at all temperatures considerably above those quoted in the paper, and although there is some falling away with decreasing temperature, there is no indication of really brittle behaviour at temperatures around the authors' indicated minimum. Additionally, no evidence of intergranular failure was evident in sections taken from the tensile specimens and examined under the microscope.

While the low elongation values obtained by Toaz and Ripling at their intermediate temperatures can be explained by a high sodium content, it is less easy to account for the comparatively high values at their two lowest temperatures, which, it will be noted, are above those obtained by us with our purer material at  $-50^{\circ}\text{C}$ . Assuming, however, that these have not been brought about by irregularities in the preliminary heat-treatment—and work by Mr. J. D. L. Eynon and myself has shown that  $\beta$  alloys of lower sodium content than those used here could, by variations in the conditions of cooling after high-temperature heat-treatment, be made to show variations in elongation of 0–40%—there would still seem to be some evidence in support of a dip in the elongation/temperature curve for magnesium-lithium alloys of low sodium content. Such a dip, however, would be much shallower than has been suggested, and further work would appear to be required to provide a full explanation.

It is a pity that this interesting work was carried out on such poor material, and it is to be hoped that the authors may have an opportunity to check their results at some later date. In this connection they may care to note that, to ensure complete freedom from the detrimental effects of sodium, we have found it necessary to hold the content of that element to a level lower by a factor of  $\times 20$  to  $\times 30$  than that of the  $\beta$  alloy which they used.

Mr. G. B. Brook,\* B.Met. (Member): It has been emphasized that the readiness with which the ternary alloys based on the  $\beta$  phase of the magnesium-lithium system over-age, even at moderately low temperatures, seriously detracts from their use as engineering materials. Nevertheless, the paper by Professor Jones and Dr. Hogg shows the alloys to be of great interest from the point of view of the effect of minor alloying additions on the precipitation process.

The authors were able to relate this effect in some way unknown to the valency of the element added. That this cannot be done in all systems can be seen by considering similar effects in copper-base alloys. In particular, much smaller quantities of beryllium (0.03 wt.-%) and antimony (0.06 wt.-%) delayed the over-ageing of a copper alloy containing 18–19% manganese and 20% nickel. Fig. G summarizes the ageing behaviour of these alloys. It is extremely unlikely that these effects in copper alloys can be related to differences in valency.

However, in many copper alloys, e.g. Cu–Ag,† Cu–Ni–Sn,‡ Cu–Be,§ Cu–Ni–Co,|| Cu–Ni–Fe,¶ Cu–Ni–Si,|| as well as Cu–Ni–Mn, over-ageing is associated with the development of “discontinuous precipitation”, a form of recrystallization induced by plastic strains occurring during precipitation and nucleated at the grain boundaries. This recrystallization spreads into the grains and produces new grains of equilibrium composition containing a more stable form of the precipitate. In Cu–Ni–Mn alloys, the small traces of beryllium and antimony both delay the onset of discontinuous precipitation

and the overageing usually associated with it; cobalt is reported to have a similar effect in Cu–Ni–Si alloys.¶ Although the actual mechanism is not known, it is probable that the trace element also affects the size to which the metastable coherent precipitate can grow before coherency

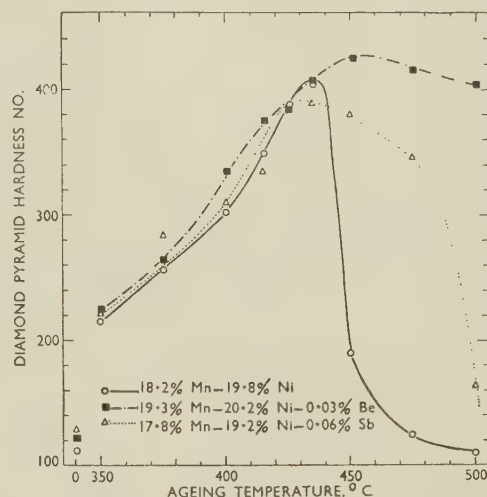


Fig. G.—Effect of Beryllium and Antimony on Hardness/Ageing-Temperature Curves for Copper-18% Manganese-20% Nickel Alloys Aged for 24 hr. at Each Temperature.

is lost. However, it is extremely unlikely that the discontinuous precipitation is the sole cause of over-ageing in these alloys.

The behaviour of these copper alloys would seem to be similar to that of the magnesium-lithium ternary and quaternary alloys studied by Professor Jones and Dr. Hogg. In particular, it would be of interest to know the minimum amounts of silver and copper required to delay over-ageing, and also whether discontinuous precipitation or grain-boundary recrystallization was observed in the authors' alloys. On p. 260 (col. 2, line 42), the authors write: “Further ageing past the point of maximum hardness produced a change in etching characteristics of the alloy... particularly at the junctions of grain boundaries ‘darkening’ occurred and these areas spread to occupy the whole grain as ageing proceeded.” This would seem to be characteristic of certain forms of discontinuous precipitation, but it is not clear from Figs. 10 and 11 (Plate LXIV) of the paper whether this was in fact so.

Dr. H. SUTTON,\*\* C.B.E., F.R.Ae.S., F.I.M. (Member): With regard to Table I (p. 257) of the paper by Professor Jones and Dr. Hogg, which shows the effect of a fourth metal on instability in magnesium-lithium-base alloys, it seems that nickel and antimony might have had a more powerful influence if they had possessed a greater solid solubility in magnesium. All the other elements in the table show appreciable solubility in solid magnesium. The effect of adding cerium, caesium, lanthanum, and rubidium might be worth examination if Professor Jones and his colleagues feel sufficiently intrigued to continue with their studies of magnesium-lithium alloys. I believe that the U.S. Bureau of Standards have found cerium additions promising. Possibly Professor Jones has seen the results of that work.

\* Head of Physical Metallurgy Section, Fulmer Research Institute, Stoke Poges, Bucks.

† F. W. Jones, P. Leech, and C. Sykes, *Proc. Roy. Soc.*, 1942, [A], 181, 154.

‡ G. B. Brook, unpublished information.

§ A. G. Guy, C. S. Barrett, and R. F. Mehl, *Trans. Amer. Inst.*

*Min. Met. Eng.*, 1948, 175, 216.

|| A. H. Geisler and J. B. Newkirk, *ibid.*, 1949, 180, 101.

¶ K. Iwase, M. Okamoto, A. Adati, and I. Suzuki, *Nippon Kinzoku Gakkai-Si*, 1938, 2, 419.

\*\* Director of Materials Research (Air), Ministry of Supply, London.

As regards the general topic of instability, warm thanks are due to the authors for their careful examination of the many factors involved. The incidence of overageing and the tendency of many of the alloys to exhibit strain-softening, recorded by Mr. Toaz and Dr. Ripling, are, to say the least, consistent.

Professor W. R. D. JONES (*in reply*): In reply to Dr. Hume-Rothery, we cannot provide much additional information concerning the structure of the  $\theta$  phase. Our X-ray studies were confined to the identification of the precipitate during ageing, and a complete structure analysis was not attempted. It was suggested originally by Busk, Leman, and Casey\* that the  $\theta$  phase in magnesium-lithium-aluminium alloys could be represented as  $MgLi_2Al$ , with a structure derived from that of the compound  $AlLi$ , which is of the  $B32$  (NaTl) type. A similar structure has been envisaged for the  $\theta$  phase in alloys containing zinc, but the distribution of the zinc and magnesium atoms in the unit cell is uncertain. The (200) reflection did not appear until the alloys had been overaged considerably (e.g. for 2 months) by which time the  $\theta$  phase was well established. This may be due simply to the fact that at first insufficient of the phase was present to cause the (200) reflection to appear on the diffraction pattern; on the other hand, an ordering of the magnesium and zinc atoms may occur as ageing proceeds, resulting in the appearance of the (200) reflection and an alteration of the symmetry. The microstructures obtained during precipitation do not support the conception that  $\theta$  is a superlattice of the parent  $\beta$  phase.

There is a great deal in what Mr. Chadwick says regarding work on new alloy systems, but when this investigation was begun some years ago the unexpectedly good ductility figures obtained in the  $\beta$ -phase alloys opened up such interesting possibilities that attention was concentrated chiefly upon them. It is appreciated that lithium may be a most useful addition to some of the magnesium-rich alloys in established use these days. In our experience the melting, casting, and forging or rolling of the high-lithium alloys present no difficulties. We are interested in the results quoted by Mr. Chadwick, which are in line with our own. These hitherto unpublished results represent a valuable addition to our knowledge. One interesting feature observed with the manganese alloys is the large elongation values in the cast state, values obtained even when the lithium used was of inferior quality as regards its sodium content. This suggests that manganese is useful in removing or mitigating the effects of sodium in lithium metal. The manner in which manganese might effect sodium removal is not established, as there are no known compounds of manganese and sodium. The mechanism suggested by Dr. Emley (whereby the  $LiCl$  liberated by the chloride fluxes out the bulk of the sodium) seems to be quite adequate. We agree with Mr. Chadwick that until the stability of these magnesium-lithium alloys is improved prospects are not encouraging.

In reply to Dr. Emley, the lithium chloride and lithium fluoride used as flux were of the highest grade available.† The sodium contents were not determined, as it was considered unlikely that sodium, even if present in the flux in appreciable amount, would increase seriously the sodium content of the alloys. A fracture test of alloys made from high-purity magnesium and lithium melted under flux did not exhibit the "crystalline" areas associated with sodium contamination. This test was used also as a quality test for each new parcel of lithium metal. With regard to the 0.3% zirconium mentioned in connection with Fig. 7 (Plate LXIII, Vol. 84) this was acid-soluble zirconium determined in accordance

with the method given by Mayer and Bradshaw.‡ Dr. Emley's suggestion that cold working an alloy containing only the stable  $MgLiX$  precipitate might be beneficial, has been considered, but in an alloy consisting only of the  $\beta$ -matrix and particles of  $MgLiX$ , any such treatment would be little more than cold working a simple binary  $\beta$  alloy, which does not improve appreciably the mechanical properties, and in fact such alloys when produced from pure materials are virtually self-annealing. Dr. Emley's discussion of the sodium-contamination difficulties is interesting. The elimination of sodium may be purely a fluxing by  $LiCl$ , as suggested, assisted by a scouring action, possibly that of liberated chlorine in the case of the manganous chloride addition. Both manganese and zirconium are sparingly soluble in  $\beta$  magnesium-lithium alloys and exist either as the elements or as particles of nitride. Sodium decreases the ductility of these alloys by forming a film at the grain boundaries. It is possible that manganese or zirconium may affect the contact angle or increase the effective strength of the film at the grain boundaries and thus mitigate the bad effect of the sodium.

We are glad to note that there is so much in common between our work and that of Mr. Payne and Mr. Eynon. We were particularly careful with regard to the sodium content of the lithium metal and satisfied ourselves by direct experiment that both sodium and potassium contents had been controlled strictly. Every new parcel of lithium metal was approved by a "fracture" test of a cast alloy, employed before a reliable method for the determination of sodium could be introduced as a routine test. The elongation value of 60% quoted for the 12% lithium alloy is not an isolated figure, and if the sodium content is very low and the melting technique good, higher figures are possible—often more than 65% and in one case a value of 87% in the cast state from remelted scrap. Elongation figures in a tensile test of forged or rolled alloys are affected by so many factors that they should not be quoted except in conjunction with the corresponding "strength" figures.

We regret that in the paper by myself and Dr. Hogg it was not pointed out that additions of other metals to the three basic ternary alloys (the compositions of which had been given in weight per cent.) had been given in atomic per cent., used because of the advantage in any discussion or explanation of the results. We agree that the effects produced by the addition of copper are somewhat surprising, as the solid solubility of copper in the  $\beta$ -phase magnesium-lithium alloys was considerably greater than might have been forecast. In the ternary  $\beta$ -phase copper-bearing alloys, single-phase structures were obtained by heat-treating alloys containing up to 3½% copper. It would have been more satisfying to have included other elements, such as indium, thallium, or manganese, in the efforts to stabilize these alloys, but considering their use in practice and the small strengthening effect of manganese on the binary  $\beta$ -phase alloy, further experiments did not seem justified. We agree that it is not unlikely that the poor resistance to creep, the tendency to overage, and the lack of stability have a common origin, and it may be profitable to try to carry out further work of a more fundamental nature which could help solve this problem.

With reference to Mr. Brook's contribution, in recent years a great deal of experimental work has been carried out on factors which may influence hardening in alloys,§ and the opinion is gaining ground that valency effects are important. However, very small amounts of added metals may exercise an effect which differs not merely in degree but in mechanism from that caused by larger amounts of the same additions. The small additions may produce a superposed effect, and their role in delaying overageing (e.g. of the copper alloy given as

\* R. S. Busk, D. L. Leman, and J. J. Casey, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, 188, 945.

† They were not available in the "Analar" grade.

‡ A. Mayer and G. Bradshaw, *Analyst*, 1952, 77, 476.

§ e.g. A. L. Norbury, *J. Inst. Metals*, 1923, 29, 407.

N. P. Allen, T. H. Schofield, and A. E. L. Tate, *Nature*, 1951, 168, 378.

D. Hardie and R. N. Parkins, *J. Inst. Metals*, 1956-57, 85, 449.



an example by Mr. Brook), and thus moving towards stabilization at an elevated temperature, could be tied up with the mechanism of increased resistance to creep mentioned by Mr. Payne and Mr. Eynon. We did not investigate the effects of the addition of very small amounts of other metals (the lowest addition was rarely less than 1 at.-%), so we have no information as to the minimum amounts necessary to produce an alloy stable at 16° C.

The "darkening" referred to in Figs. 10 and 11 (Plate LXIV) is due not to a form of discontinuous precipitation but rather to a darkening of existing particles of precipitate, which we suggested was due to a change in composition of the precipitate; the darkening took place while the lattice parameter of the  $\theta$  phase was decreasing. In no case was a form of precipitate observed in these alloys which might be termed discontinuous.

We are interested in the contribution by Dr. Sutton, particularly in view of the great interest and help he has shown in our work. The effect of cerium and/or Mischmetall (which includes lanthanum) on the binary magnesium-lithium alloys was so small that it was not considered profitable at the time to add metals of the rare earths to the ternary alloys in any attempt to decrease instability. Any further work in this direction could possibly include the addition of rarer metals, but it is considered that the prospects are not very promising.

Mr. TOAZ and Dr. RIPLING (*in reply*): The possible influence of sodium on these tests, as stressed by Dr. Emley and by Mr. Payne, is, of course, mentioned in the paper.

Of especial interest to us were the additional data presented by Mr. Payne on the low-sodium magnesium-13% lithium alloy. Although only four points were obtained for this material, the data again appear to describe a ductility minimum at about the same temperature as that shown in Fig. 5 (p. 139) for the slow strain-rate tests. This might indicate that these alloys do indeed always exhibit these ductility depressions (possibly because all of them contain some sodium), and the magnitude of the depression may be a function of the sodium content.

That Mr. Payne found "no evidence of intergranular failure" does not mean that fracturing did not start at the grain boundaries.

These ductility minima, as opposed to general low-temperature brittleness, are not uncommon. For example, one of us (E. J. R.) found that a titanium-0.085% nitrogen alloy displayed a low-temperature recovery much like that shown here for the  $\beta$  alloy. The ductility testing/temperature behaviour of this material is shown below:

Testing Temp.		Ductility (Contraction-in- area, %)
°F.	°C.	
-321	-196	70
-200	-129	52
-110	-79	46
R.T.	R.T.	40
+200	+93	40
+400	+204	43
+600	+315	53
+800	+427	80

## Discussion

### Fatigue of Copper\*

Dr. B. CINA,† B.Sc., Ph.D. (Member): Before further work is undertaken or reported on the effect of "high-stress" fatigue testing on copper or other metals, I suggest that careful consideration be given to just what such "high stresses" involve. Mr. Kemsley and his co-workers ‡§ have drawn attention to the marked difference observed by metallographic and X-ray diffraction examination between low- and high-stress-fatigued copper test-pieces, and in the first paper (p. 417) he discusses the variations in their hardness and structural changes on subsequent annealing. Low stresses are of the order of  $\pm 11,000$  lb./in.<sup>2</sup> and high stresses from  $\pm 20,000$  to  $\pm 25,000$  lb./in.<sup>2</sup>. The author has nowhere given a nominal tensile stress/strain curve for his material. However, some idea of the strains corresponding to these stresses can be obtained by calculation from published stress/strain data on annealed copper of comparable quality. Allowing for some variation in grain-size between the different materials, the strain involved would be somewhat as shown in Table A.

The extent of strain involved is significant at all stress levels and particularly so at the so-called "high stresses". It is not surprising that the surfaces of the high-stress-fatigued test-pieces were rumpled. This surely means that within a few cycles after reaching the maximum applied load, an accurate knowledge of stress was no longer attained. From Voce's data,¶ a nominal stress of  $\pm 25,000$  lb./in.<sup>2</sup> would have given a true stress of  $\pm 28,500$  lb./in.<sup>2</sup>. Allowing for a stress-concentration effect at the foot of the valleys

resulting from the rumpling (see Mr. Kemsley's second paper), the true stress would have been still greater than  $\pm 28,500$  lb./in.<sup>2</sup>.

From the facts: (a) that X-ray-diffraction photographs gave complete rings from high-stress-fatigued samples, as

TABLE A.

Nominal Stress, lb./in. <sup>2</sup>	Strain, %		
	Voce ¶	French and Hibbard **	Marshall and Shaw ††
11,000	2	> 3 *	> 1.6 *
20,000	8	> 8.1 *	> 6.2 *
25,000	14	> 13.2 *	> 8.7 *

\* Only true-stress/true-strain data were provided. As the maximum true stresses in the fatigue tests would have been greater than the nominal ones because of the plastic deformation induced, the strain figures calculated above are underestimated, possibly by as much as 40% at the higher stress values.

did a tensile specimen stretched 10%; (b) that hardness attained after "fatigue" at  $\pm 20,000$  and  $\pm 25,000$  lb./in.<sup>2</sup> was also very akin to that of the tensile specimen; (c) that striations could be detected in low- but not in high-stress-fatigued samples, nor in the tensile specimen; and (d) that

\* Joint discussion on two papers by D. S. Kemsley published in the *Journal* (this vol., pp. 417 and 420).

† Brown-Firth Research Laboratories, Sheffield.

‡ R. B. Davies, J. Y. Mann, and D. S. Kemsley, *Internat. Conf. on Fatigue of Metals (Inst. Mech. Eng.)*, 1957, 551.

§ D. S. Kemsley, *J. Inst. Metals*, this vol., p. 153.

¶ D. S. Kemsley, *Phil. Mag.*, 1957, [viii], 2, 131.

¶ E. Voce, *Metallurgia*, 1955, 51, 219.

\*\* R. S. French and W. R. Hibbard, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, 188, 53.

†† E. R. Marshall and M. C. Shaw, *Trans. Amer. Soc. Metals*, 1952, 44, 705.

recrystallization did not occur on annealing in low- but did occur in high-stress-fatigued samples, as in the tensile specimen, it would seem a not unreasonable conclusion that high-stress-fatigued samples were, in fact, dynamically cold worked on loading to, and within a few cycles after reaching, the maximum load. Thereafter, fatigue was carried out on a dynamically cold-worked surface, but one can hardly describe the structural and hardness changes observed after fatigue testing as being due to high-stress fatigue, since the changes induced in the material were probably not derived from the cycles of high stress but from cycles of increasing stress on loading. To demonstrate that his high-stress tests were significant, the author should surely have uniformly cold worked his test-pieces, preferably in a single dynamic pulse \* to the same maximum stress as in his high-stress fatigue tests, and machined his fatigue test-pieces from such dynamically cold-worked material.

It is not denied that hardening can occur during fatigue, but it is important to distinguish between such genuine hardening, developed without significant overall changes in dimension of the test-piece, and that developed by applying excessive loads which simply dynamically cold work the test-piece and bring about significant changes in dimension on loading to the maximum stress.

Mr. R. C. GIFFKINS,† B.Sc., F.I.M., (Member): Mr. Kemsley has noted in the second paper under discussion that as many as 50% of the crack paths near the fracture of fatigue specimens of copper run along the boundaries of annealing twins; he had previously found these boundaries to be preferred sites for the formation of the striations revealed by special etching reagents on repolished sections of copper fatigue specimens.‡§ Since twin boundaries are coherent, this preference is somewhat surprising. However, it has been observed|| that tilting can occur about annealing-twin boundaries during creep, the tilting apparently being associated with fine slip. Kuhlmann-Wilsdorf and Wilsdorf\*\* have also noted that the boundaries of annealing twins may act as barriers to slip in more rapid deformation. The tilting observed during creep would result from different amounts of slip in the grain and its twin or, in other words, would arise if the twin boundary traps dislocations predominantly of one sign. In this way the coherent twin boundary may be converted into a low-angle tilt boundary. This process would obviously be favoured by creep conditions, since at normal rates of tensile testing there is more possibility of slip crossing the boundary by a burst-through of dislocations, whereas during creep there is a greater likelihood of dislocation climb taking place.

A similar conversion during fatigue would provide a reason for the preferential formation of striations and cracks at annealing-twin boundaries. It cannot be said whether this then constitutes a source of fatigue cracks or merely a preferred path for cracks already initiated by some other mechanism, such as that proposed by Louat and discussed by Mr. Kemsley in the first paper under discussion and elsewhere.‡ In this connection it should be noted that Kemsley's photomicrographs show slip parallel to twin boundaries in both grains and their twins; this is in contrast to the slip in normal tensile specimens which is usually of a characteristic "herring-bone" pattern. Possibly, dislocations involved in slip parallel and near to a converted annealing-twin boundary could become locked by the dislocations of this (tilt) boundary, and so provide the cores of dislocations postulated by Louat.

THE AUTHOR (*in reply*): Dr. Cina's basic criticism is that the results obtained at high stress do not reflect the changes produced by such a stress on annealed material, since cold working is introduced during the loading sequence. This is, of course, true of both low- and high-stress specimens, and is unavoidable in any fatigue test. Dr. Cina then suggests that initial cold working of the specimens at the maximum stress to be applied in later testing would be necessary to demonstrate the significance of the high-stress results. While I agree that such an experiment should be undertaken, I would point out that the present work was an attempt to provide some knowledge of the metallographic features associated with the normal laboratory method of fatigue testing, in which any initial variation in specimens is undesirable. The results are therefore quite significant in this context, particularly if they lead to a re-assessment of the value of the high-stress region of the  $S/N$  curve. I have not overlooked facts (a)-(d) listed by Dr. Cina, as will be seen in my conclusion that "as the (cyclic) stress increases, the deformation becomes less localized and more like that produced by unidirectional stress".

I agree with Dr. Cina that an accurate knowledge of stress conditions is not available in high-stress copper specimens because of surface rumpling, but this is also true of any fatigue specimen as soon as cracking begins. We are woefully ignorant at present as to how early in the life this may occur. I have not overlooked the stress concentration which occurs in the foot of the valleys, and have indeed used this concept to account for the intercrystalline cracks in rumpled specimens.

Mr. Giffkins has suggested a possible reason for the high proportion of cracks associated with annealing twin boundaries in low-stress specimens which seems quite plausible.

\* F. P. Bullen, A. K. Head, and W. A. Wood, *Proc. Roy. Soc.*, 1953, [A], **216**, 332.

† Physical Metallurgy Section, C.S.I.R.O., University of Melbourne, Australia.

‡ D. S. Kemsley, *J. Inst. Metals*, this vol., p. 153.

§ D. S. Kemsley, *Phil. Mag.*, 1957, [viii], **2**, 131.

|| R. C. Giffkins, *J. Inst. Metals*, 1953-54, **82**, 39.

\*\* D. R. Miller, M.Sc. Thesis, Melbourne University, 1953.

\*\* D. Kuhlmann-Wilsdorf and H. Wilsdorf, *Acta Met.*, 1953, **1**, 394.



## Discussion

## Pseudo-Subgrain Structures on Aluminium Surfaces

By N. C. WELSH

(Journal, this vol., p. 129)

Mr. E. C. W. PERRYMAN,\* M.A., A.I.M. (Member): Dr. Welsh has clearly shown that the subgrain structures so often seen on electropolished and chemically polished surfaces are not connected with the metallurgical structure. Since the interpretation of such structures is so important, I should like to give some further evidence which supports the author's findings.

While working on the subgrain structures formed in super-purity aluminium after cold working and recovery, I was trying to find a surface preparation which would reveal the subgrains quickly and unambiguously. The technique being used was to electropolish, chemically etch, and examine under a phase-contrast microscope. The chemical etch was such that small differences in level were produced between adjacent subgrains, thereby giving contrast under the phase-contrast microscope. The size of subgrains observed by this procedure depended on the amount of cold working, the purity of the metal, and the annealing temperature, and it agreed with the subgrain size determined by an X-ray micro-beam technique. Samples of widely different subgrain size ( $1-5\mu$ ) were chemically polished by the same technique as that used by Hunter and Robinson† and examined with the electron microscope. Substructures similar to those observed by Hunter and Robinson were found, and the size of the subgrains was the same for all specimens. It is clear, therefore, that the subgrains observed by Hunter and Robinson are pseudo-subgrains and are not connected with the metal structure.

During an investigation into the reason why certain anodizing procedures rendered an electropolished aluminium surface apparently optically anisotropic, it was concluded that this was because the anodizing process altered the surface topography, producing striations similar to those observed by Dr. Welsh but more widely spaced. At that time, we examined a sample supplied by Dr. G. A. Geach which showed striations after electropolishing and, in fact, had a structure similar to that shown in Fig. 7 (Plate XXII) of the author's paper. This sample was found to be slightly optically anisotropic, that is, there was a slight contrast between grains when examined under polarized light. In some of the samples which Dr. Welsh examined, the striation spacing was as great as  $3000\text{ \AA}$ , and I should like to ask whether he found any relationship between the striation spacing and the optical anisotropy of the polished surface. If the spacing could be increased, it would be possible to examine the grain structure without having to introduce the extra step of anodizing.

Dr. WELSH (*in reply*): Mr. Perryman's observation that surface structures of the type discovered by Hunter and Robinson on chemically polished aluminium are independent of the normal subgrain size is certainly a strong indication that these structures, like those formed during electropolishing, are pseudo-subgrains. It is, however, necessary to distinguish clearly between the two types of structure, with only one of which my paper was strictly concerned. The principal reason for believing that the electropolishing structures are artefacts, viz. that they change in pattern and spacing as the conditions of electrolysis are varied, cannot, of course, apply to structures formed without applied e.m.f., as in chemical polishing. Furthermore, the polygonal markings

observed by Hunter and Robinson were generally coarser than the patterns formed during electrolysis, ranging in spacing from  $0.2$  to  $1\mu$ , according to the purity of the aluminium.

I have not studied the topography of chemically polished surfaces, but, as mentioned in the paper, I have observed structures closely resembling those of Hunter and Robinson while operating at low potentials in the hydrofluoric acid-alcohol-water bath (see Fig. 24, Plate XXIII), and by simple immersion of the metal in this and other electrolytes. An example of the structure formed by prolonged immersion in the phosphoric acid-alcohol-water bath is shown in Fig. A (Plate LXXXIV), and it is evident that this is quite distinct in character from the simple, cellular patterns which formed during electrolysis in the same bath (cf. Figs. 19-22, Plate XXIII). While these markings were undoubtedly similar in shape and size to the markings described by Hunter and Robinson, observation of the mode of structure formation led to an interpretation differing from that of those authors. The polygon boundaries, which Hunter and Robinson considered to be grooves selectively attacked by the chemical reagent, were found to be ridges separating shallow pits. The markings in fact appeared to develop by the merging of small, separately nucleated etch pits, as evident in Fig. B (Plate LXXXIV), where structure formation is complete only on one grain. This interpretation is significant, as it is unlikely that the polygon boundaries could be regions of lattice misfit, as Hunter and Robinson supposed, and yet be relatively resistant to etch attack. It is also pertinent to note that on near-(110) faces the polygons were invariably elongated in the  $\langle 100 \rangle$  directions. According to the subgrain hypothesis this characteristic would imply crystal anisotropy, a surprising attribute for which there is no independent evidence. The directional shape is, I suggest, simply another manifestation of the directional surface-etching behaviour responsible for the greatly attenuated "furrow"-type markings which form under some conditions of electrolysis (see Figs. 7, 9, 15, and 23, Plates XXII and XXIII).

Although it seems most improbable that the structures formed without applied e.m.f. portray directly the shape and size of misoriented subgrain blocks (a conclusion supported by Mr. Perryman's observations), it must be admitted that certain findings of Hunter and Robinson do favour the existence of some form of substructure in the metal crystals. For example, it is claimed that cold working caused fragmentation and distortion of the structure and that in a quenched and aged aluminium-magnesium-silicon alloy precipitation of  $Mg_2Si$  particles occurred primarily along the "subgrain" boundaries. It is important that these claims should be scrutinized and the full significance of this type of structure ascertained.

I regret that I have made no study of the optical anisotropy of electropolished surfaces. It is possible, as Mr. Perryman suggests, that the grain structure could be revealed by this means, though I would point out that under the particular conditions I employed the maximum spacing of the striated ("furrow") pattern was only about  $2000\text{ \AA}$ . "Dotted", "globular", and "granular" patterns developed with greater spacings, but it is doubtful whether these would produce the optical anisotropy required.

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† M. S. Hunter and D. L. Robinson, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, 197, 717.

## Discussion

# Effect of Internal Oxidation on the Tensile Properties of Some Silver Alloys at Room and Elevated Temperatures

By E. GREGORY and G. C. SMITH

(Journal, this vol., p. 81)

Dr. R. HAYNES,\* B.Met., Ph.D., A.I.M. (Member): In an investigation of the mechanism and conditions under which hydrogen embrittlement occurs in commercially pure silver and dilute silver alloys, specimens were prepared of commercially pure silver of a purity similar to that described in the paper, and alloys containing nominally 0.2 wt.-% aluminium and 0.2 wt.-% copper. Before embrittling treatment in hydrogen, specimens were annealed in air for 24 hr. at 800° C. After this treatment, neither commercially pure silver nor the aluminium-bearing alloy showed any sign of a precipitate, but the copper-bearing alloy exhibited large globules of a blue-coloured oxide randomly distributed throughout the silver matrix. These observations were in accord with the authors' comments regarding the effect on the size of the oxide particles formed of the difference between the free energies of formation of the solute and solvent.

Subsequent annealing in hydrogen, at the same temperature and for the same time, resulted in severe embrittlement of the commercially pure silver and of both alloys, by the formation of randomly distributed cavities in the metals, as had been found previously by Chaston.† In the copper-bearing alloy, the oxide particles formed during the oxidation period disappeared during the hydrogen anneal, being replaced by cavities, presumably filled by water vapour at the annealing temperature. Thus, it appeared that one possible cause of hydrogen embrittlement was the reduction of oxide particles formed during internal oxidation; however, other factors also may be operative. It is clear from these few results that the addition to commercially pure silver of small quantities of aluminium, which forms an oxide much more stable than that of hydrogen, is not adequate to preclude embrittlement of internally oxidized silver in hydrogen-bearing atmospheres.

Chaston † also showed that very high-purity silver was

not embrittled under similar conditions, indicating that commercially pure silver is probably susceptible to internal oxidation. It would be of interest to know whether the authors carried out experiments on commercially pure silver and, if so, whether improvements in the tensile properties due to internal oxidation were noted.

The AUTHORS (*in reply*): The silver used in our experiments was 99.99% pure, the chief residual impurities being iron and copper. No experiments were made using commercially pure silver. Dr. Haynes's remarks are extremely interesting, however, as we did investigate to a small extent the effect of reheating internally oxidized specimens in different atmospheres, although we did not mention these results in our paper. The experiments were restricted to a silver-0.13% silicon alloy oxidized at 650° C. and then reheated in atmospheres such as nitrogen, oxygen, hydrogen, at temperatures from 600° to 850° C. Very severe embrittlement was produced by heating in hydrogen at 650° C. and to a slightly less extent at 850° C. We explained this on the basis of the formation of water vapour by hydrogen reduction of the oxides of the trace elements iron and copper, formed during the internal oxidation. A small amount of reduction of silica may also have taken place, but we have no experimental evidence for this. We did not study the effect of reheating in hydrogen internally oxidized silver-aluminium specimens.

In view of Dr. Haynes's results, it would be of interest to make a more detailed study of the effect of annealing in hydrogen internally oxidized silicon- and aluminium-containing alloys. It may well be that the factors controlling the reduction of the oxides in such cases differ from those operating during the reduction of isolated massive oxides, and that some reduction of silica and alumina may occur and be responsible for the observed embrittlement.

## Discussion

## Liquid Metals ‡

Dr. IVOR JENKINS,§ F.I.M. (Vice-President) (*Rapporteur*): As far as I am aware this is the first occasion on which we have had an opportunity of discussing, as a general theme, the basic properties and behaviour of liquid metals as such. The reason for this is not far to seek. As in other fields, the growing importance of nuclear energy has brought a stimulating and often refreshing outlook to old or dormant problems, and the papers under discussion describe work which has been prompted primarily because of the growing importance of liquid metals in the nuclear-energy field. Increasing interest has been shown in the potential use of liquid metals in heat-exchange systems in various branches of engineering

and in advanced types of nuclear reactor, and this interest has stimulated the need for a rapid build-up in our basic knowledge of such systems in order to keep pace with the rapid technological developments in these various fields.

Mercury is so commonplace in the laboratory and elsewhere that it is perhaps as well that the paper by Mr. Strachan and Mr. Harris should remind us that it is a liquid metal. Their paper describes, as a result of simple experimentation, the attack of a large number of unstressed metallic elements and certain alloys in static liquid mercury over prolonged periods of time at room temperature and at 500° C. When attack occurs, it involves the wetting of the metal surface by

\* Imperial Chemical Industries, Ltd., Metals Division, Birmingham.

† J. C. Chaston, *J. Inst. Metals*, 1945, 71, 23.

‡ Joint discussion on the following papers published in the *Journal*: J. F. Strachan and N. L. Harris (this vol., p. 17); M. F.

Jordan and D. R. Milner (p. 33); A. G. Ward and J. W. Taylor (p. 145); D. A. Melford and T. P. Hoar (p. 197).

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the mercury, amalgamation, and solution, and in certain cases, particularly with nickel, intergranular penetration. Whether the attack on nickel as shown in Fig. 3 (Plate V) is characteristic of the metal itself or is associated with the particular grain-boundary conditions obtaining in the nickel used, may be brought out in discussion.

The interesting observation is made that, in the presence of air, oxidation of the dissolved element will result in precipitation from solution, and so can lead to a form of mass transfer. In view of this, it may be felt that it would be useful to know the solubility of oxygen in mercury at the temperatures used in the investigation, and, in particular, whether this was likely to have in any way influenced the results of the investigation.

The authors reach the conclusion that the attack under static conditions, as represented by solubility determinations, shows a periodic relationship with the atomic number (as shown in Fig. 2, p. 22), and suggest that this may be related to the nature of the electronic shell structure. There would appear to be some justification for this conclusion, when it is noted that the solubilities of the elements in B sub-groups with completed *d* shells exceed those of other metals, whilst of the latter, the transition group shows the least attack. However, the authors do not elaborate on this point, and there would appear, from Fig. 2, to be a number of exceptions to their general conclusion. This would seem to be an obvious point for discussion.

Mr. Ward and Dr. Taylor consider that one of two factors limits the rate of solution of solid copper in liquid lead and in liquid bismuth, namely the rate of dissolution of copper atoms into the liquid or the subsequent rate of diffusion of copper atoms through a boundary layer at the surface into the bulk of the liquid. It is argued by the authors that the variation of the solution-rate constant with temperature is inconsistent with the view that the limiting mechanism is the solution rate at the copper/liquid interface, but that it is consistent with the limiting mechanism being the rate of diffusion through the laminar boundary layer. On the other hand, whilst this viewpoint can be reconciled with the experimental findings for the copper/lead system, it is not so for the copper/bismuth system, and the authors conclude that the disagreement in the latter case is associated with convection effects affecting the thickness of the laminar boundary layer due to the greater solubility of bismuth in copper.

Bearing in mind the relative densities of bismuth and copper, on the one hand, and lead and copper, on the other, it may be not unreasonable to expect that, if natural convection effects resulting from local changes in density do occur, they should not be insignificant in the copper-lead system. However, perhaps this debatable point will not be resolved until it is possible to measure by direct experiment the magnitude of any convection effects. Certainly it would be interesting to know whether superimposed convection currents, induced perhaps ultrasonically or electromagnetically, would help to clarify the significance of the experimental results obtained in the present work. In this respect, the results of Strachan and Harris, showing that dynamic conditions accelerate attack by liquid mercury, may be significant.

A further interesting conclusion from this investigation is that, if the results for both systems are expressed on a curve relating, on the one hand, the ratio of concentration to saturation concentration, and, on the other, time to time for saturation, common curves are obtained for each system covering all temperatures and that these curves are in themselves identical. This is of particular value, since limited data on the equilibrium concentration at any one temperature and the time taken to reach that equilibrium will immediately define the system. It would be interesting to consider to what extent this principle can be applied to systems which

are not as simple as those covered by the present paper, for example, the systems studied by Strachan and Harris, and, in particular, what might occur when the solid phase is an alloy.

The paper by Dr. Melford and Dr. Hoar describes a new and improved technique for the determination of the surface tensions of molten lead, tin, and indium up to about 1000° C. Certainly it would seem that this method is less susceptible to human error than any employed hitherto, but a new technique, because of its novelty, should provoke discussion, and no doubt this will arise, particularly perhaps in regard to the purity of the metals used and their environment during test, and the authors' assessment of the magnitudes of the various errors involved in the investigation.

An interesting observation is that tests with lead-tin and lead-indium alloys give results intermediate between those of the pure metals, and it is claimed that this may be regarded as additional evidence supporting the reliability of the data obtained. The case for this is not clearly made, and would justify some discussion.

From the surface-tension data the authors have calculated the molar surface entropies, and in Table I (p. 203) compare these with the corresponding molar bulk entropies. In all cases the surface entropies are small compared with the properties in bulk, and the authors draw from this the conclusion that the surface layers of the liquid metals are less ordered than within the bulk, but nearer that of the liquid bulk than the gaseous phase. Disorder in the surface is stated to increase more rapidly with temperature than bulk disorder. Further, the low molar surface enthalpy in relation to the latent heat of evaporation is taken as an indication that the bonds on an atom at the surface have a mean strength greater than those in the bulk liquid. These are very interesting and debatable points which strike at the very fundamentals of the structure of liquid metals.

There have been important advances in recent years in the brazing of aluminium and its alloys, and the effectiveness of the process has been closely associated with the development of various fluxes for the removal of the natural oxide film on the metal. The paper by Dr. Jordan and Mr. Milner goes a long way towards clarifying the mechanism whereby oxide is removed by the flux.

The investigation has shown that the flux produces attack at a large number of centres in the metal grains, some of which are more susceptible than others, and that, in general, the oxide film at the grain boundaries is more difficult to remove. The reason for this is not obvious, and merits discussion, particularly since the investigation also shows that the rate of attack decreases with increasing purity of the aluminium.

The picture presented by the authors assumes that the first stage in the removal of the oxide is the penetration of it by the flux through local inhomogeneities in the film. The authors do not comment on the nature or causes of these defects, and it is not clear whether they visualize these as being lattice imperfections or macro-defects. If they exist on a lattice scale, it would be interesting to discuss the mechanism of flux diffusion through them. If, however, they exist on a macro-scale, it would be interesting to speculate on whether they are of a sufficient magnitude to permit ready access of the flux to the underlying surface, and whether at the base of such defects the metal surface is exposed. This is a most interesting aspect of this paper.

It is claimed that the results of the investigation are equally applicable to alloys. Some may wish to speculate on whether alloying may affect the physical characteristics of the oxide film and whether this in turn may affect the fluxing action.

Dr. B. R. T. FROST,\* B.Sc. (Member): Liquid metals are of practical interest in the fields of heat transfer, joining (i.e.

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soldering, brazing, and welding), and casting. The requirements and problems in the heat-transfer field are unique and are distinct from those in the casting and joining fields. In the last two cases the metal is usually molten only for a short period of time and the melt is held at a constant temperature or the bulk is fairly uniformly cooled; in these processes solidification (nucleation and growth) and the study of interfacial conditions are important. In heat transfer the metallic coolant is molten for very long periods of time and is circulated round systems having large differences in temperature in different sections. Consequently, reliability over long periods is required and attention is focused on temperature-gradient/mass-transfer effects. These in turn are sensitive to the levels of solubility of the container materials in the coolant metal and to the rates at which these levels are attained. In addition, the precipitation of solute material at the coldest part of the system is of considerable importance and has tended to be neglected in mass-transfer studies.

Another fact relevant to this discussion is the emphasis on the heavy metals in these papers. The behaviour of bismuth, mercury, and lead in engineering systems is very different from that of sodium, potassium, or lithium. The former dissolve much greater quantities of common structural materials (iron, chromium, nickel, &c.) than do the latter, and, moreover, they display greater tendencies for intergranular penetration.

The papers fall into two groups: two dealing with solution processes in mass transfer and two dealing with surface or interfacial phenomena.

The two papers on solution processes, (those by Mr. Ward and Dr. Taylor, and by Mr. Strachan and Mr. Harris) are illustrative of the need for information on equilibrium solubility levels, on their variation with temperature, and on the rate at which equilibrium is approached before one can begin to attempt to predict rates of mass transfer. Reference to Fig. 5 (p. 147) of Ward and Taylor's paper amplifies this point. Considering the purely hypothetical case of a copper loop round which bismuth is circulated through the temperature difference between 510° and 410° C., it is obvious that the driving force for mass transfer is the difference between the equilibrium solubilities at the two temperatures. At 510° C. the copper dissolves in a few minutes up to a value corresponding to saturation at 410° C. Thereafter the kinetics of mass transfer will be controlled by the rate of precipitation from the supersaturated solution, and one suspects that the overall rate of mass transfer in flowing-liquid-metal circuits is usually controlled by the precipitation or plugging process rather than by the solution rate. Studies of the kinetics of plug formation, following the admirable pattern set by Turnbull, are essential in this field.

I should like to make the following comments on the paper by Mr. Strachan and Mr. Harris:

(i) While I agree with the authors that weight-loss measurements are inadequate for solubility determinations, I do not think that chemical analysis overcomes this difficulty. The undissolved particles are often so small that complete removal would be possible only with a filter so fine that the liquid would take a very long time to pass through it. The one absolutely reliable method is to make use of some property which is affected only by atoms in true solution. Such a property is the e.m.f. generated between a solution and the pure solvent, as is measured in thermodynamic-activity studies. Dr. Strickland-Constable, in the Chemical Engineering Department of Imperial College, is using this technique for mercury alloys quite successfully.

(ii) Solution can occur without the liquid/solid contact angle falling below 90°, whereas intergranular penetration leading to removal of grains cannot occur under these conditions. In these circumstances one could accept solubility measurements with some confidence.

(iii) Various theories of solubility have been proposed. Dr. Eldred has applied Hildebrand's solubility parameters to the problem, and Dr. Kerridge has observed that solubility levels are a function of the solute elements rather than the solvents.

An alternative approach might be through the dislocation theory of liquids. Dr. Smallman, at Harwell, has postulated from X-ray-diffraction data that a liquid metal contains about  $5 \times 10^{13}$  dislocations/cm.<sup>3</sup>, i.e. 1 dislocation every 50 atoms, corresponding to crystallites a few atoms wide in accordance with the X-ray picture of rapidly decreasing order beyond nearest neighbours.

A 5% solution corresponds to 1 solute atom/dislocation, and a 5 p.p.m. (atomic) solution to 1 atom/ $10^4$  dislocations. Although lattice strain is essentially absent from a liquid and the mobility of ions is high, it may be that solute-atom/dislocation interactions, which are so important in solid metals, may also provide a clue to solubility relationships in liquids.

(iv) The oxidation effects might be explained by the segregation to the top of the mercury of easily oxidized compounds, when the capsules were cooled. No solubility of oxygen is required in this case.

It has been found that uranium-mercury compounds floating on mercury oxidize very rapidly even in supposedly pure argon or in all but the highest vacuum (i.e. below  $10^{-5}$  mm. Hg).

(v) Cavitation in liquid bismuth has been observed with and without ultrasonic vibrations. A bismuth-filled thermal-convection loop to which a transducer had been attached showed marked pitting after application of 25-kc. oscillations from a 500-W. generator. The tips of the steel impeller of a liquid-bismuth pump showed cavitation effects similar to those observed in ships' propellers. This effect can be eliminated by providing greater pressure on the suction side of the pump by imposing a gas pressure over the system.

Dr. Melford and Dr. Hoar are to be congratulated on producing a modification of the capillary-rise technique for surface-tension measurement which eliminates a number of errors. Their criticism of other methods, on the grounds that oxidation would be more troublesome, does not apply if similar conditions of vacuum and atmosphere to those used by the authors are employed. It may well be that other workers have not, in fact, been as careful as they were.

I should like to know whether the theory of increased disorder and concentration of vacancies at the surface of a liquid has special significance at a solid/liquid interface. Essentially, all methods of measurement of surface tension involve solid/liquid interfacial tensions and a solid/liquid interface will be analogous to a solid/solid grain-boundary interface where misfit permits concentration not only of impurity atoms but also of dislocations or vacancies. This fact, coupled with the very irregular nature (on the atomic scale) of even the smoothest surfaces, e.g. glass tubing, means that the solid and liquid atoms have only a limited opportunity of getting sufficiently close together to exert their maximum interaction forces. In commenting on the co-ordination number of particles in the surface, the authors state that this is 9, compared with 12 in the bulk. X-ray studies show, with a fair degree of reliability, that the co-ordination number lies between 8 and 10, even at temperatures close to the melting point. With additional vacancies at the surface an atom may have an average co-ordination of less than 6. This does not substantially alter the argument explaining the values of  $H\sigma/\lambda E$ , but it gives added weight to the point that one should consider the mass effect of attractive forces due to free electrons rather than the interaction with nearest-neighbour cations.

Dr. D. H. KERRIDGE\*: In connection with the paper by Mr. Strachan and Mr. Harris on the solubility of metals in

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mercury, I should like to say something about a correlation found by Dr. C. C. Addison and myself in 1953 at Nottingham University.

Using solubility values previously published, chiefly for binary diagrams, we have shown, using 19 liquid metals as solvents, that the solubility in a particular solvent at a constant temperature varies in a regular periodic fashion with the atomic number of the solute. We find that the maxima on the solubility/atomic-number curves occur at the same solutes, regardless of the solvent metal or temperature used. The solutes in question were those with the lowest latent heat of fusion and the lowest melting point, i.e. the alkali metals and manganese, gallium, indium, mercury, and bismuth. These solutes are not the same as those shown in Harris and Strachan's paper (Fig. 2, p. 22), because their values differ considerably, in some cases very considerably, from those of other workers.

The striking similarity between all the plotted solubility/atomic-number curves and those for latent-heat-of-fusion/atomic number, suggested the possibility of a quantitative correlation. This was found to resemble the classical thermodynamic equation for ideal solubility:

$$\ln x = \frac{L_f}{R} \left( \frac{1}{T_m} - \frac{1}{T} \right)$$

where  $x$  is the mole fraction at temperature,  $T$ , of a solute of latent heat of fusion  $L_f$  and melting point  $T_m$ .

If, to a first approximation, the entropy of fusion can be regarded as a constant, then the logarithm of solubility is proportional to the latent heat at a constant temperature.

Plots of log solubility against latent heat of fusion of solute gave a rather broad spread of points, but the gradient of lines joining solutes of atomic numbers differing by one varied fairly closely around an average value. This average altered to some extent with the position of the solute in the Periodic Table. For  $d$ -block solutes, i.e. those with an unfilled  $d$ -shell of electrons, the average gradient is  $RT$ , as predicted by the classical equation. For  $p$ -block solutes the value is  $RT/2$ .

As would be expected, the solubility does not follow the thermodynamic equation exactly. The constant term in the equation varies for different solutes.

However, it has proved possible to predict unknown solubility values by extrapolating from the known solubility of nearby solute metals, the accuracy diminishing with the distance apart of the unknown and reference solutes. For neighbouring solutes, the predicted value is normally in the range 0.7–1.7 of the experimental value.

Attempts are being made to improve the correlation by incorporating other terms. Modification by including a Hildebrand internal-pressure term or an electronegativity term similar to that used by B. W. Mott\* has not proved fruitful.

It is hoped to publish the complete data in which this correlation is used in the near future.

Dr. A. K. COVINGTON,† B.Sc., and Dr. B. W. HOWLETT,† B.Sc. (Member): We are interested in the systems, copper/lead and copper/bismuth, studied by Mr. Ward and Dr. Taylor. We have recently observed one copper–bismuth and three copper–lead compounds forming below 500° C. and previously unreported. We presume that these compounds cannot exist above the lowest temperature at which solution-rate studies were carried out (360° C. in the system with bismuth, 410° C. in that with lead). Solution processes, in cases where inter-metallic compounds exist in the system at the temperature of the investigation, would not show the simple form found by

Dr. Taylor. We should like to ask Dr. Taylor whether he observed any of these compounds in microscopic sections, and whether rate studies were made at any temperature below those reported. We should also like to direct the first question to Dr. Eldred, although he makes no mention ‡ of having sectioned his drained liquid metal.

Dr. V. W. ELDRED,§ M.A., A.I.M. (Member): I was particularly interested in the paper by Mr. Ward and Dr. Taylor because the technique used is one which I developed at the Department of Metallurgy, Cambridge, in 1950 and applied to a number of solid/liquid metal systems. The results of that work which have been described and discussed in detail elsewhere,‡ drew special attention to the importance of convection currents in the dissolution process under nominally static conditions, and I should like to comment on the present results from this point of view.

Expression (2) (p. 146), with which the results are consistent, was originally derived for the case of a solid dissolving in a well-stirred liquid. It is based on the assumptions that the thickness of the diffusion layer is constant with time and uniform over the surface, and that, at any given time, the concentration of solute in the bulk of the liquid is uniform. Since such conditions are unlikely to apply in a static test, even under the influence of convection, it would be of interest to know whether the authors have been able to explain why the same type of expression is applicable in these circumstances. Concentration/time curves which I obtained with the copper/lead system at 400° and 500° C., using a volume: area ratio of 1.2 cm., do not quite fit expression (2); in effect, the solution-rate "constant"  $K$  itself appears to decrease with increasing concentration of solute in the liquid. This suggests that the precise form of the dissolution curve may generally depend on the volume: area ratio in a more complex manner than is indicated by this equation.

Wagner|| derived an expression for the rate of solution of a vertical solid surface in a large volume of liquid when controlled by diffusion and convection. It is tempting to modify this expression to allow for the varying concentration of solute in the liquid when the volume of the latter is limited, but it does not seem possible to derive expression (2) in this way, even if possible concentration gradients in the bulk of the liquid are ignored. There is, however, an important observation, not mentioned by Mr. Ward and Dr. Taylor, which makes it clear that factors additional to those covered by Wagner's equation are involved. This is the fact that with both copper/lead and copper/bismuth the attack on the copper rod is more severe near the surface of the liquid than at the bottom. Such tapering of specimens is encountered with many systems and is probably due primarily to the steadily increasing thickness of the diffusion layer as it moves upwards or downwards over the vertical surface in the convection process. In many cases it is possible to predict whether the maximum attack will occur at the top or the bottom of the specimen from the relative densities of the solid and liquid (e.g. with the aluminium/tin system the attack is most severe at the bottom). The copper/lead and copper/bismuth systems are, however, exceptional: from the enhanced severity of attack at the top it may be deduced that the density of the fluid immediately adjacent to the copper surface during dissolution is greater than that of the bulk of the liquid. I originally suggested that this might be a result of local cooling due to the heat of solution, and I wonder whether the authors have looked further into this possibility.

In view of these uncertainties, do the authors agree that it would be unwise to assume that the same velocity constants of solution, or even the same form of dissolution expression,

\* *Phil. Mag.*, 1957, [viii], 2, 259.

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‡ V. W. Eldred, *Atomic Energy Research Estab. Rep. No.*

002

X/R1806, 1956.

§ Research and Development Branch, U.K. Atomic Energy Authority, Windscale Works, Cumberland.

|| C. Wagner, *J. Phys. Colloid Chem.*, 1949, 53, 1030.



will necessarily apply when different geometric arrangements or volume/area ratios are involved?

In the discussion of results (p. 150), it is suggested that the plots of reduced concentrations ( $n_i/n_0$ ) against reduced times ( $t/t_0$ ) are of particular interest. Surely, however, there is no special significance in these, since such a result must follow once an exponential relationship has been established?

Dr. Covington and Dr. Howlett have reported the discovery of intermetallic phases in the copper-lead and copper-bismuth systems. I carried out several metallographic examinations of drained metal from both systems and also inspections of the surfaces of the dewetted specimens, but in no case were any new phases detected. A possible explanation may be that the specimen tubes were all cooled so rapidly after inversion that the formation of these phases was suppressed.

Mr. J. MACKOWIAK,\* B.Sc.: During a recent investigation on the dissolution of solid titanium in molten aluminium, I realized that the surface of the dissolving solid decreased appreciably with time. A review of the literature concerned with the dissolution of solid metals in liquid metals gives the impression that this factor has been completely neglected. It seems to me that one is not justified, in cases where the dissolution process is controlled by diffusion or by diffusion and convection, in taking as the measure of the rate of dissolution the increase in concentration of the dissolving metal, unless the change in surface area is negligible.

I have made a simple calculation which shows that the percentage change in the area of any cylindrical specimen, neglecting  $\Delta x^2$  terms, is:

$$\Delta S = \frac{\Delta x (h + 3r) \cdot 100}{r(h + r)}$$

where  $\Delta S$  = percentage change in total surface area,  $\Delta x$  = change in length of  $r$  or  $h$  measured at time  $t$ ,  $r$  = radius of the specimen, and  $h$  = height of the specimen.

From this equation it can be seen that even small changes in the linear dimensions of the specimen may produce, in certain geometrical cases, an appreciable error, if the increase in concentration of the dissolved metal is taken as a measure of the dissolution rate. In addition, it is clear that the concentration of the dissolved metal in the liquid, under identical conditions of temperature and time, will be a function of the ratio of the radius,  $r$ , to the height,  $h$ , of the specimens used. This error will be systematic and will become more important at higher temperatures, where the solubility is greater. It follows that in such cases the energies of activation obtained, using the same experimental method and the same materials but specimens of different size, would vary unless corrections were made.

In view of the fact that Mr. Ward and Dr. Taylor used an experimental method in which the total surface area of the specimen changed continuously and because of the previously discussed difference between the concentration/time graphs obtained by the authors and those of Dr. Eldred, I should like to ask them if they could give any data regarding the extent of dimensional changes in their specimens.

Mr. A. CALVERLEY,† B.Sc.: My contribution to the discussion concerns a determination of the surface tension of liquid tungsten, using the drop-weight method.

Experience with electron-bombardment floating-zone melting‡§ shows, only too well at times, that it is easy to produce liquid drops of refractory metals. It was natural therefore to investigate whether or not the apparatus described§ was adaptable to drop-weight determinations of surface tension.

By removing the lower half of a rod set up for floating-zone melting and substituting for it a molybdenum cup, we found that drops could be formed on the lower end of the upper half of the rod, caught in the cup, and weighed. By applying a correction factor due to Harkins and Brown, by allowing for thermal expansion of the rod, and by estimating the liquid density of the drop, a value for the surface tension of the drop can be calculated. To assess the method, a single determination for copper was made and a value of 1150 dynes/cm. was obtained; this compares well with the value of 1140 measured by the maximum-bubble-pressure method in hydrogen and taken from the "International Critical Tables".

The value obtained for tungsten is 2300 dynes/cm.  $\pm 5\%$  at its melting temperature in a vacuum of approximately  $10^{-4}$  millibars.|| The method is obviously applicable to many other refractory metals, but I have not made any measurements on them. The method, as it stands, does not permit of a study of the variation of surface tension with temperature.

It is hoped to publish full details of the work on tungsten later.

The Admiralty are thanked for permission to make this contribution.

Mr. STRACHAN and Mr. HARRIS (*in reply*): Before replying individually to the various points raised, we should like to emphasize that our paper presents the results of a general survey, rather than a detailed investigation of the attack of the metallic elements and of various engineering alloys by liquid mercury. Accordingly, the simplest possible experimental techniques, applicable to a wide range of metals, had to be employed. We are well aware of the difficulties inherent in some of the techniques used, as commented on by Dr. Frost, and indeed discuss these in some detail in our paper. Towards the end of our programme of work, we carried out a few preliminary trials on electrical-conductivity and contact-resistance methods of determining solubility, but owing to the pressure of other commitments these experiments had to be stopped. Particulars of this and of other parts of the work discussed in our paper, including some typical microstructures, the omission of which from the paper was especially regretted by Dr. Eldred, are given in a further report,¶ declassified since the paper was published.

The point raised by Dr. Jenkins concerning the attack on nickel at 500° C., as illustrated in our Fig. 3 (Plate V), is important, since nickel can suffer severe intergranular penetration and loss of strength without excessive weight loss. As the material used in our tests was "low-gas" strip containing a minimum of 99.35% nickel, it is possible that the attack observed was associated with impurities in the grain boundaries. In reply to Dr. Jenkins' further comments, the solubilities of oxygen and nitrogen in mercury at the temperatures used are very low, so that the solubility of air would not influence our results. However, the possibility of traces of air being entrapped in the mercury by the specimens, as was observed in some of the earlier experiments, might indeed have influenced the results. It was mainly to eliminate this possibility that the high-vacuum techniques described in the paper were employed.

Dr. Frost has raised some other interesting points. We have not attempted to apply any of the current theoretical ideas on liquid solutions to our results. The purpose of our Fig. 2 (p. 22) is to demonstrate the periodic nature of the solubility of the metallic elements in mercury, and perhaps to encourage fresh thinking on the subject. Whilst we agree that the mechanism suggested by Dr. Frost may explain the oxidation effect, we also feel that the solute atoms may themselves oxidize on exposure to air and thus come out

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‡ M. Davis, A. Calverley, and R. F. Lever, *J. Appl. Physics*, 1956, 27, 195.

§ A. Calverley, M. Davis, and R. F. Lever, *J. Sci. Instruments*,

1957, 34, 142.

|| A. Calverley, *Proc. Phys. Soc.*, 1957, [B], 70, (11), 1040.

¶ J. F. Strachan and N. L. Harris, *Atomic Energy Research Estab. Rep.*, 1954, (X/R1503).



of solution. We entirely agree that no solubility of oxygen is required, and indeed have not offered this suggestion. We are well aware that cavitation can occur without ultrasonic vibrations and that the phenomenon may be suppressed by the application of pressure. The main point we wished to bring out was that cavitation could in fact take place in a liquid metal under the appropriate dynamic conditions as well as in water, and that the subsequent erosion could be very serious indeed, even at temperatures where there was no evidence of attack under static conditions. We are interested that Dr. Frost has confirmed our observations with ultrasonic vibrations in the case of liquid bismuth. It might be worth mentioning that the ultrasonic technique was originally intended as a means of removing surface oxide films from our specimens, as is claimed to occur, for example, in the ultrasonic soldering of aluminium. However, the pitting and erosion which occurred with every metal tested was so severe that we abandoned this method. In many cases the specimens were not only pitted but were also riddled with holes.

We note that Dr. Kerridge and Dr. Addison have found, from a study of published data, that the variation of solubility is also periodic for other liquid metals. Dr. Kerridge's brief summary of their work and of the relations found is important, and we await with great interest the publication of their paper on this matter. With respect to Dr. Kerridge's remarks on discrepancies between our peak solubility points and the maximum values given in the literature for certain elements in mercury, we would like to emphasize again the discussion in our paper of the experimental difficulties involved. In particular, we wish to point out that any previous determinations of solubilities in mercury carried out in the presence of air could be completely invalidated by the marked tendency for the solutes to oxidize and come out of solution. This difficulty also applies to some extent in our own work, since, although we recognized this aspect of the problem at an early stage and carried out our experimental runs under high-vacuum conditions, the actual filtering before chemical analysis was carried out in the usual way under ordinary atmospheric conditions. We suggest in our paper that in future investigations this problem might be overcome by filtering under an inert atmosphere, although we note with interest Dr. Frost's remarks on the rapid oxidation of uranium-mercury compounds, even in supposedly pure argon.

Dr. JORDAN and Mr. MILNER (*in reply*): Dr. Jenkins has raised various questions about the early stages of the oxide removal, particularly the penetration of the film, on which we should like to make a few brief comments.

The initiation of the flux attack, involving the setting up of local cells at the oxide/metal interface, is obviously a very complex problem, and insufficient information has been obtained so far in the present work to permit a detailed model to be established. Macro-defects in an oxide of the type formed on aluminium are extremely unlikely, and it is suggested that the initial points of attack are lattice imperfections in the film. Clearly this rules out penetration by the flux itself, and it is envisaged that the first stage in the attack is the passage through the film of the flux anions,  $F^-$  and  $Cl^-$  ions. Penetration of the naturally formed oxide on aluminium by the fluoride- and chloride-type ions is an accepted fact in corrosion studies, where it is considered to occur by an exchange mechanism with the oxygen ions in the film. The behaviour of the metal grain boundaries in retaining remnants of the oxide film, rather than forming the first points of attack, is admittedly more difficult to explain, but may be due to a concentration of cathodic areas at the grain boundaries.

In suggesting that the findings might also apply to aluminium alloys, we did not intend to include all alloys under all conditions, but only those for which fluxes of the type under

investigation were known to be effective. This would exclude, for example, those alloys having a high magnesium content.

Mr. WARD and Dr. TAYLOR (*in reply*): We shall reply to Dr. Jenkins' and Dr. Eldred's comments jointly since a number of points are common to both.

Dr. Eldred attaches considerable importance to the tapered form of specimen which resulted from his experiments and suggests that this indicates the existence of complicating factors in the dissolution process. We did not detect this effect in either of the systems studied, to the gross extent he implies. The diameter of a copper specimen immersed in liquid lead for  $41\frac{1}{2}$  hr. at  $510^\circ C.$  (i.e. for a period sufficient to ensure equilibrium solubility) varied by less than  $\pm 0.0015$  in. along the attacked length. We also disagree with Dr. Eldred that his observation of tapering outwards to the bottom is indicative of the copper solutions being necessarily denser than the pure solvents; an increase in density of the former over the latter would surely imply extremely strong association in the liquid state, which is hardly justified on the basis of the accepted phase diagrams.

We have not considered the heat-of-solution effect referred to by Dr. Eldred, but feel that any such phenomenon is likely to be swamped by other thermal effects of a practical nature and by the good thermal conductivity and convection conditions existing in the system.

Dr. Eldred refers to an expression derived by Wagner for the rate of solution of a vertical solid surface in a liquid, when the process is controlled by diffusion and convection. This expression was evaluated for conditions applying in the first few minutes of the present dissolution studies, when the thickness of the diffusion layer can be expected to be reasonably uniform. The following is a comparison of the corresponding calculated and experimental solution rates:

Temp. $^\circ C.$	Solution Rate, moles/cm. <sup>2</sup> /sec. $\times 10^7$	
	Calc.	Exptl.
<i>Pb/Cu System</i>		
410	1.41	0.52
460	1.77	1.76
510	2.68	3.16
<i>Bi/Cu System</i>		
360	2.93	3.84
410	6.98	6.80
460	18.5	14.30
510	29.4	24.2

The reasonably good agreement between the calculated and experimental values appears to confirm that diffusion and convection are rate-determining factors in the initial stage of dissolution in both systems. Owing to the higher solubilities in the copper/bismuth system, the convection effects are greater than in copper/lead, a point raised by Dr. Jenkins. It appears unlikely that the mechanism of dissolution would alter from one of diffusion and convection at the start of the process to some other, e.g. to one controlled by atom transfer at the solid/liquid interface, at a later stage.

If the dissolution mechanism is, in fact, controlled by convection and diffusion of the solute in the liquid, the process is mathematically analogous to that in which a cylindrical volume of gas, contained by a perfect thermal insulator, is heated by a central hot wire, operating at constant temperature  $T_H$ , from some initial temperature  $T_0$ , to  $T_H$ . Woodrow\* has evaluated rigorously expressions for the thermal case corresponding to the exact geometry which we employed, and for two distinct conditions:

(i) Laminar flow in the fluid with no convective turbulence. This case corresponds in the dissolution process to one controlled entirely by the diffusion of the solute in the solvent.

(ii) Turbulent flow conditions introducing a convective

\* J. Woodrow, unpublished work, Atomic Energy Research Establishment, 1957.

transfer component. This case corresponds to dissolution by a combined diffusion and convection mechanism.

For the copper/lead system at 410° C., the expressions corresponding to conditions (i) and (ii) were:

$$\begin{aligned} \text{(i)} \quad \bar{C}/C_0 &= 1 - 0.90 \exp(-10.4Dt). \\ \text{(ii)} \quad \bar{C}/C_0 &= 1 - 0.90 \exp(-62.3Dt). \end{aligned}$$

The corresponding experimental relationship derived from the present studies was:

$$\text{(iii)} \quad \bar{C}/C_0 = 1 - 0.90 \exp(-61.5Dt),$$

where  $\bar{C}$  = average solute concentration at time  $t$  after the start of the test,  $C_0$  = saturation solute concentration at any fixed temperature, and  $D$  = diffusion coefficient of the solute in the solvent.

The fact that the relationship in (i) indicates a solution rate much lower than the experimental value (expression (iii)) means that diffusion alone is too slow to account for the observed experimental values. The satisfactory agreement between expressions (ii) and (iii) is taken as further evidence for regarding the solution process as one of diffusion and convection due to density differences in the liquid accompanying the dissolution. Similar agreement was obtained at the other temperatures and with the other system studied.

We agree with Dr. Eldred that it would be unwise to attempt in any way to apply the present laboratory-scale results to a system having a different geometry and experimental conditions without further experimentation. Results obtained on the present systems under dynamic conditions\* and on the iron/bismuth system under static conditions† suggests that a similar form of expression may be applicable.

Dr. Eldred correctly points out that the  $(\eta_t/\eta_0)/(t/t_0)$  relationships follow from the exponential relationship established. The particular significance and utilitarian nature of these expressions is illustrated in another paper.\*

In reply to Dr. Covington and Dr. Howlett, we found no evidence of compound formation in either system during the solution-rate studies, but no direct attempt was made to detect any such formation on cooling, since the entire liquid-metal sample was employed for chemical analysis after the test. No tests were made at temperatures below those reported in the paper.

We infer from our results that any such compounds were unstable at the test temperatures employed, for the following

reasons. Perfectly consistent and constant saturation-solubility values were obtained in both systems at all temperatures, for tests of duration as long as 66 hr. in some cases. Had compound formation occurred, it is extremely unlikely that this consistency would have been preserved. Furthermore, as a general rule, intermetallic compounds are readily wetted by the solutions with which they are in equilibrium, and there is frequently a tendency for such compounds to spall off into the liquid owing to volume changes, disregistry, &c. Finally, our equilibrium solubility values agree well with those determined independently by Kleppa and Weil‡ for the lead/copper system over the temperature range of interest.

Mr. Mackowiak raises an interesting point regarding the change in surface area of the specimen during dissolution, and in this connection one must clearly distinguish between purely geometric, or macro-surface, and micro-surface areas. According to Mr. Mackowiak, the greatest percentage change in total surface in the present studies, i.e. for the bismuth/copper system at 510° C., was less than 10% and became negligible in the other cases. On the other hand, the specimen surfaces after test frequently appeared roughened on a micro-scale, so that while the geometric surface area may decrease, the effective surface area undergoing solution may remain constant or may actually increase as a result of this roughening effect; the latter is difficult to evaluate experimentally.

One of us (J. W. T.) would like to indicate that Mr. Calverley's value for the surface tension of tungsten is in good agreement with a value of 2680 dynes/cm. predicted from some cohesive-energy data.§

Dr. MELFORD and Dr. HOAR (*in reply*): With regard to Dr. Jenkins's comment about our results for lead-tin and lead-indium alloys, it is true that we have only briefly referred to them as further evidence for the reliability of the method. The full data are given in another paper.|| There it is shown that not only are the results for the alloys intermediate between those for the two pairs of pure metals, but that both the surface free energies and the surface entropies obtained for the alloys are consistent with a detailed treatment of the two binary mixtures as regular solutions of which the enthalpies of mixing have been determined by calorimetric methods. It is most unlikely that the very consistent results for two series of binary alloys could have been obtained without a very reliable experimental method.

## Discussion

## Creep ¶

MM. J. PLATEAU, \*\* C. CRUSSARD \*\* (Member), and A. CONSTANT: \*\* The work of Mr. Nield and Professor Quarrell has interested us greatly. The results of these authors can be related to some outlined briefly below, which were obtained at IRSID during a study of the hot deformation of two single-phase steels; one a stabilized austenite containing Cr 10, Ni 35, and C 0.03%, and the other a soft iron with 0.003% C. †† For each steel at least three different grain-sizes were examined.

In the case of the austenitic steel, it was possible to determine without difficulty the range of equi-cohesion temperature by a number of methods, principally depending upon:

(i) A comparison of tensile or creep-test curves obtained at a fixed temperature on test-pieces having different grain-sizes.

(ii) A study of the variation of the reduction in area of test-pieces broken in tension, as a function of the testing temperature (Figs. A and B).

\* A. G. Ward and J. W. Taylor, *J. Inst. Metals*, 1957-58, **86**, 36.

† A. G. Ward and J. W. Taylor, unpublished work, Atomic Energy Research Establishment, 1957.

‡ O. J. Kleppa and J. A. Weil, *J. Amer. Chem. Soc.*, 1951, **73**, 4848.

§ J. W. Taylor, *Metallurgia*, 1954, **50**, 161.

|| T. P. Hoar and D. A. Melford, *Trans. Faraday Soc.*, 1957, **53**, 315.

¶ Joint discussion on the following papers published in the *Journal*: D. McLean and M. H. Farmer (this vol., p. 41); D. McLean (*ibid.*, p. 468); H. Brunner and N. J. Grant (*ibid.*, p. 77); W. Betteridge and A. W. Franklin (*ibid.*, p. 473); B. J. Nield and A. G. Quarrell (*ibid.*, p. 480).

\*\* Institut de Recherches de la Sidérurgie (IRSID), Saint Germain-en-Laye (S. et O.), France.

†† R. Tamhankar, Thesis, Univ. Paris, 1957.



(iii) A study of the residual elongation at  $-196^{\circ}\text{C}$ . of wires previously broken in high-temperature tensile tests (Fig. C).

(iv) An examination of the appearance of the rupture surfaces; these are principally ductile below the equi-cohesion temperature and mainly intergranular above this temperature.

The combined outcome of these tests leads to consistent results. The equi-cohesion temperature determined by

characteristic is of assistance in determining the equi-cohesion temperature and, in particular, the reduction of area remains high even at elevated temperatures.

If one considers the change in the reduction of area as a function of temperature, it can be seen that the behaviour of the austenitic steel is very close to that of the aluminium-manganese alloy, studied by Nield and Quarrell, while the

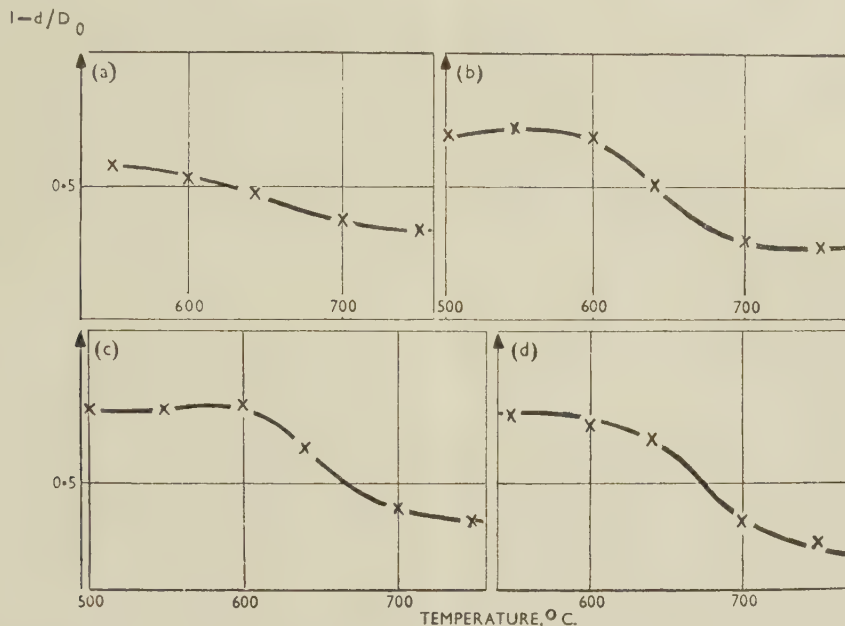


FIG. A.—Variations of  $(1 - d/D_0)$  as a Function of Temperature for Different Grain-Sizes of Stainless Steel.

(a) Grain No. 6; (b) grain No. 8; (c) grain No. 10; (d) grain No. 13. (A.S.T.M. scale).

$d$  = dia. of minimum section at rupture.

$D_0$  = initial dia. of test-piece.

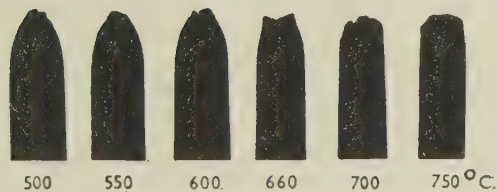


FIG. B.—Test-Pieces Broken at Various Temperatures.

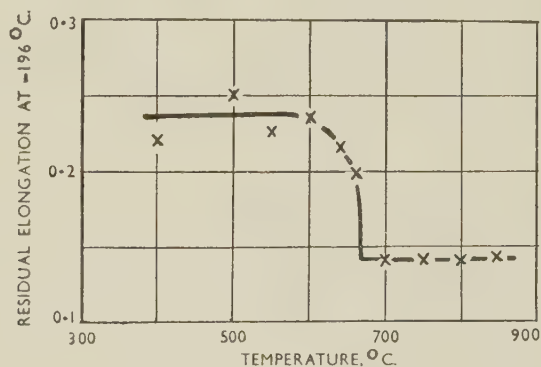


FIG. C.—Residual Elongation at  $-196^{\circ}\text{C}$ . of Specimens of Austenitic Steel Broken in High-Temperature Tensile Tests, as a Function of the Original Test Temperature.

examination of the broken specimens is close to  $660^{\circ}\text{C}$ . This differs little from that determined from the true stress reached for a given elongation, when the latter is not far removed from the elongation to fracture, which proves that the inter-crystalline decohesion is directly controlled by grain-boundary sliding.

The same tests have been carried out on the soft iron, but with very different results. At about  $550^{\circ}\text{--}600^{\circ}\text{C}$ ., inter-granular slip takes place, as revealed by internal friction measurements and by micro-examination, while the appearance of the rupture becomes intergranular. But no other

iron resembles more the aluminium-magnesium alloy at  $300^{\circ}\text{C}$ .

X-ray-diffraction and micrographic examination of the two steels led to conclusions similar to those reached by Nield and Quarrell to account for these differences of behaviour.

(1) With the iron, the appearance of intergranular sliding is accompanied by marked grain-boundary migration (Figs. D and E, Plate LXXXV) and also by almost complete polygonization (Fig. F, Plate LXXXV). The degree of disorientation is very great near the grain boundaries (up to  $20^{\circ}$  for high elongations). Intergranular sliding can cause

the appearance of deformation bands in the neighbouring grains, oriented in the direction of the grain boundaries along which sliding occurs (Fig. G, Plate LXXXV).

(2) With the austenitic steel, the intergranular sliding is not accompanied by any new phenomena, very little grain-boundary migration takes place at high temperatures, and polygonization is always imperfect. At about 750°–800° C., the appearance of an intergranular precipitate may help to prevent the migration (as in the case of the aluminium-manganese alloy).

One can say, therefore, that in the case of iron the phenomena accompanying the reorganization of the lattice, polygonization and migration of boundaries, mask the onset of "equi-cohesion"; it appears clearly, however, in the austenitic steels, where these phenomena do not interfere. This result is analogous to that obtained by Nield and Quarrell, who, in comparing two light alloys, have shown a similar influence of grain-boundary migration on the reduction of area, mode of fracture, and the residual elongation.

Dr. McLean has observed fissures of type (a)\* above a certain value of the load: 15 tons/in.<sup>2</sup> for Nimonic 80A, and 5–8 tons/in.<sup>2</sup> for the other alloys which he studied; and fissures of type (b)\* below 7 tons/in.<sup>2</sup> for Nimonic 80A and 5 tons/in.<sup>2</sup> for the other alloys.

One wonders whether the load is the only determining factor in the appearance of the fissures observed; it is our opinion that temperature and time must also play an important part in their initiation and development. Jenkins and Jenkinson† have shown that the phenomena of recovery, recrystallization, and grain-boundary migration which take place during creep can influence the formation and propagation of cracks. Since these phenomena are dependent on temperature and time, it seems reasonable to conclude that the formation of fissures and their changes during test should also depend on these two factors.

Considering the results obtained by Dr. McLean and taking into account the phenomena of recovery, recrystallization, and migration mentioned above, one can interpret in the following manner the two types of cracks observed:

Type (a) corresponds to a range of time and temperature (taking into consideration the high loads applied) where the processes of recovery, recrystallization, and migration are not greatly involved; while type (b) corresponds to conditions of temperature and time where these processes can play an important part.

On the subject of the influence of modifications of the lattice during creep, one of us (C. C.), developing theories published earlier‡ on the interaction of crystalline dislocations with "boundary dislocations" and its influence on boundary glide or migration, has recently presented a paper entitled "Study of Structural Modifications of Steel during High-Temperature Deformation".§

With regard to the two types of crack observed by Dr. McLean, and remembering the eventual roles of the phenomena of recovery and migration, it seems that yet another factor should be taken into consideration. This concerns the possible action of fine intergranular precipitates formed during creep on the development of cavities of type (b), and we should like to ask Dr. McLean whether he has been able to detect such precipitates in relation to cavities of this type. Since it is not very easy by the usual methods to observe fine intergranular precipitates in a test-piece that has undergone creep and above all at the surface of a crack, we suggest

the use of the techniques of microfractography, which consists of the examination of broken surfaces by the electron microscope. The micrographs are obtained from direct carbon replicas.¶ In the case of creep, the method can be applied with success to ruptures at high temperature, if the test takes place in a neutral atmosphere or in a vacuum. Fig. H (Plate LXXXVI) illustrates the intergranular precipitate which forms during creep in the austenitic steel mentioned above in discussing the paper by Mr. Nield and Professor Quarrell. The method can be applied also to the detection and observation of cavities produced during creep. By rebreaking at low temperatures a test-piece that has undergone creep and taking a microfractograph, one can easily distinguish, in the zone of intergranular rupture, those cracks which were formed at high temperature, because they are distinguished by oxidation markings similar to those shown in Fig. H.

If intergranular precipitates form, during creep, it is probable that the life of the corresponding test-pieces would be relatively high. At least, that is what one would deduce from the equation given by Dr. McLean (p. 471):

$$\sigma^2 \geq \frac{12\gamma G}{\pi L}$$

because, irrespective of the variations in the term  $\gamma$ , the distance  $L$  which intervenes should then be the mean distance between the two precipitates.

Has Dr. McLean recorded any results which would enable him to say whether this is the case? In any event, we find a typical example in the work of Dr. Betteridge and Mr. Franklin. From the tests of these authors, the appearance of an intergranular precipitate corresponds with an increase in the life of the test-piece. However, our interpretation of this effect differs from that of Betteridge and Franklin, the two alternative hypotheses being as follows: (i) The essential part is played by the depletion in chromium of the area in the neighbourhood of the precipitates; and (ii) the precipitates constitute in some part anchoring points for the two adjacent grains with respect to each other and in this manner they decrease the stresses at the triple points. In order to try to decide between these hypotheses, we suggest a study of the zones low in chromium, using the electronic probe micro-analyser which allows local analyses to be made on areas of 1–2  $\mu$  dia.

Finally, we should like to mention a method derived from microfractography which permits of the identification of fine intergranular precipitates, and which we have in particular applied to the case of Nimonic alloy. It involves making a replica of the surface of the intergranular rupture, and then in identifying the precipitates by diffraction, localized or otherwise. In the present case, test-pieces of Nimonic (after normal industrial heat-treatment) were broken at low temperature, and gave intergranular fracture; the precipitate, which we were able to identify by means of 12 lines, seemed to be  $M_{23}C_6$ , rather than  $M_7C_3$ .

Mr. R. EBORALL,¶ M.A. (Member): Before discussing the papers on fracture, I should like to raise one point on Dr. McLean and Mr. Farmer's paper on grain-boundary sliding. The authors have now amassed quite a lot of evidence that in a polycrystalline specimen the grain-boundary movement under a wide range of conditions is controlled by ordinary crystalline slip. To explain this finding, they put forward ideas which depend on the main obstacle to grain-boundary sliding being very small irregularities in the boundary. Of

\* Type (a) are wedge-shaped cavities based on a grain corner. Type (b) are isolated cavities occurring anywhere along a boundary.

† C. H. M. Jenkins and E. A. Jenkinson, *J. Iron Steel Inst.*, 1957, 185, 23.

‡ C. Crussard and J. Friedel, "Creep and Fracture of Metals at High Temperatures", p. 243. 1956: London, (H.M. Stationery Office).

§ C. Crussard and R. Tamhamkar, paper presented to the American Institute of Mining and Metallurgical Engineers at Chicago, November 1957.

¶ J. Plateau, G. Henry, and C. Crussard, *Rev. Univ. Mines*, 1956, (ix), 12, 543.

¶ Head of General Metallurgy Section, British Non-Ferrous Metals Research Association, London.



course, some irregularities are likely to be present, but is it not more probable that in a polycrystal the main barrier to movement occurs at the ends (three-grain junctions) of the moving boundary? If the ends are pinned, full elastic relaxation occurs after a very small amount of sliding, and the larger movements observed here necessarily involve plastic deformation of the grains abutting on the ends of the boundaries, as shown for instance by Chang and Grant\* and by Dr. Betteridge and Mr. Franklin in another paper.† It could thus be supposed that the normal situation in creep was that the shear stresses at the boundaries were fully relaxed, and the sliding at the grain boundaries was controlled almost entirely by the crystalline creep of the grains at the ends. At lower temperatures partial relaxation only might occur. No doubt this picture is over-simplified, but I feel finality has not been reached.

As regards intercrystalline fracture, Dr. McLean's beautiful metallography seems to show quite clearly, as he suggests, that either of the types of mechanism proposed can be operative; at high stresses the Zener type of mechanism holds and the stress concentration due to grain-boundary sliding leads to cracking from grain corners, and at low stresses the Greenwood vacancy-condensation mechanism is the one that causes failure. Another example of the Zener mechanism, in which the necessity for a three-grain junction (or its equivalent) to produce stress concentration has been definitely shown, has been given recently by Dr. Harper.‡ He showed for  $\beta$ -brass at 400° C. that a specimen containing a single three-grain junction in its width could readily be broken in this way, but that a bicrystal with a flat boundary normal to the axis could not be made by any simple means to crack along the boundary.

There is an interesting point in Dr. Betteridge and Mr. Franklin's paper. They say that it is an advantage to have a small amount of a soft phase at the grain corners to dissipate the stress concentration. This may be the explanation of a curious fact about brasses: a high-tensile cast  $\beta$ -brass is prone to intercrystalline cracking on prolonged stressing, but the presence of a little  $\alpha$ , which is softer, removes this susceptibility, and propeller brasses accordingly always have to contain at least 15%  $\alpha$ . It is necessary to be cautious, however, about advocating structures containing soft phases at the grain boundaries; if there is a soft grain-boundary film which is very thin, it can itself cause intercrystalline failure even in an ordinary tensile test, because by yielding in shear it produces a stress redistribution of the kind which causes the Zener type of failure in creep. This can happen, for example, through "discontinuous" precipitation in certain aluminium alloys, and it must evidently be guarded against in age-hardening alloys generally.

Something which does not seem clear is the role of stress-concentration effects in the vacancy-condensation mechanism. It would be interesting to perform experiments on bicrystals in the appropriate range of stress, to see whether failure can occur without stress concentration.

With regard to the paper by Mr. Nield and Professor Quarrell, I am not at all clear what their proposed mechanism is. In Section IV. 3 (a) (p. 486) they seem to propose what is really a mechanism of stress concentration by grain-boundary sliding, although they have previously cast some doubt on such mechanisms. It seems as though they are applying it to small irregularities on the sliding boundaries (i.e. the oblique boundaries) rather than to the transverse boundaries. When one looks at their illustrations, however, it appears that the cracks or holes are in fact mainly on the

transverse boundaries. Perhaps they would like to clarify this point.

These authors appear to discard vacancy condensation as a mode of failure because of the low activation energy, and they emphasize the importance of grain-boundary migration as a means of relieving stresses and so preventing cracking. While not wishing to minimize the importance of the latter effect, I should have thought the low activation energy was not necessarily inconsistent with a vacancy-condensation mechanism, since the vacancies are already created by the deformation and have only to diffuse. On the other hand, the authors seem to have established grain-boundary sliding as a prerequisite for failure, so that the position seems rather confused.

Dr. J. HESLOP §: I have recently carried out metallographic work similar to that of Dr. McLean on fractured creep test-pieces of Nimonic alloys. There seems little doubt that under certain conditions rupture occurs by the joining together of voids, as described by Dr. McLean. The appearance of such voids cannot always be explained, at least in the Nimonic alloys, by chance of sectioning. The work of Machlin|| and of Balluffi and Seigle¶ has shown that condensation of vacancies to form voids is at least feasible, provided that nuclei are already in existence.

My own observations on Nimonic 90 do not indicate that stress alone determines whether failure is by grain-corner cracking or void formation. The critical stress is dependent on temperature, being about 20 tons/in.<sup>2</sup> at 650°, 14 tons/in.<sup>2</sup> at 750°, and 9 tons/in.<sup>2</sup> at 870° C. This conclusion is derived from the examination of a large number of creep specimens with rupture times from  $\frac{1}{2}$  hr. to 22,000 hr.

Stress, as such, may only indirectly control the type of rupture by influencing creep rate and hence the rate of generation of vacancies by intersecting dislocations. The rate of growth of voids by vacancy diffusion to existing nuclei would be expected to be both time- and temperature-dependent, and this is in fact observed. At 650° C. voids are not detected in specimens ruptured in less than 15,000 hr., whereas at 870° C. they are observed after about 30 hr.

Two further interesting points have arisen from this work. First, intergranular rupture by void formation is found to be much more ductile than that by the grain-corner mechanism. Secondly, it is thought that massive carbide particles at the grain boundaries act as nuclei for the voids to form on. Perhaps Dr. McLean would like to comment on these observations.

Dr. J. WEERTMAN,\*\* (Member): I wonder whether the interesting law found previously by Dr. McLean and Mr. Farmer (sub-grain size = grain-boundary sliding/deformation within the grains) should so soon be completely abandoned. Admittedly, this law is not obeyed in all the tests of the present paper, but is not the break-down of the law simply due to the fact that a stress/temperature region has now been reached where the boundaries must undergo excessive and unreasonable amounts of sliding if the law is to remain valid? The analysis by Brunner and Grant †† would suggest an upper limit to the relative amount of sliding at any grain boundary.

Dr. J. C. CHASTON,‡‡ B.Sc. A.R.S.M., A.Inst.P., F.I.M. (Member): All these papers are concerned, in one way or another, with one of the oldest problems in creep—why a metal should, so to speak, suddenly decide to give up the

\* H. C. Chang and N. J. Grant, *Trans. Amer. Inst. Min. Met. Eng.*, 1952, **194**, 619.

† W. Betteridge and A. W. Franklin, *J. Inst. Metals*, 1951–52, **80**, 147.

‡ S. Harper, *ibid.*, this vol., p. 415.

§ The Mond Nickel Co., Ltd., Birmingham.

|| E. S. Machlin, *Trans. Amer. Inst. Min. Met. Eng.*, 1956, **206**, 106.

¶ R. Balluffi and L. L. Seigle, *Acta Met.*, 1957, **5**, 449.

\*\* U.S. Naval Research Laboratory, Washington, D.C., U.S.A.

†† H. Brunner and N. J. Grant, *J. Inst. Metals*, this vol., p. 77.

‡‡ Manager, Research Laboratories, Johnson, Matthey and Co. Ltd., Wembley, Middlesex.



struggle to resist the applied creep stresses and should part bodily by a more or less extensive pattern of cracking.

This phenomenon, of course, is essentially that which has, for so many years, made it necessary to carry out long-term creep tests and has rendered extrapolation from short-term tests unreliable.

The valuable and very careful observations reported by Dr. Betteridge and Mr. Franklin on the complex alloy Nimonic 80A (p. 479) show quite clearly that: "The manner of precipitation of chromium carbide has an important influence on the amount of creep extension which occurs before fracture . . . It seems likely that the effect of the precipitation of carbide is to produce, around the boundaries, zones which are impoverished in chromium and therefore, reduced in strength. These zones permit the relaxation of stresses which, in creep, are known to concentrate at the boundaries, particularly at triple points, and which otherwise would lead to the formation of cracks".

There is, I suppose, nothing very new in this view, but it may be worth emphasizing some points which are becoming more and more clearly established:

(a) First, perhaps, less attention is being given in these days to grain-size as a factor in determining creep rate. Although very obvious, it is sometimes forgotten that grain-size in this connection must be related to size of specimen. Fig. J (Plate LXXXVI) shows what can happen when a fairly thin platinum wire is subjected to creep stresses. Clearly, if the wire were much thicker, the free sliding which is observed would be hindered, and there would be little, if any, tendency for the wire to "offset".

(b) It is of interest to see how the conception of a grain boundary is widening. It is not necessarily now thought of as a zone a few Ångströms thick. In some alloys, as in heat-treated Nimonic 80A, a wide altered zone—altered in composition as well as in crystal structure—characterizes the grain boundary. Even in relatively pure commercial metals, it seems likely that it extends much further than was thought a few years ago.

(c) If the views of Betteridge and Franklin are accepted, the objective of those who are developing strong, creep-resisting alloys, free from the tendency to crack, will be to find a means of balancing the strength of the crystals (perhaps by a type of continuous precipitation) with the strength of boundary regions of controlled width (perhaps by some form of discontinuous precipitation of a coarser particle size, coupled with localized solid-solution hardening).

With regard to the methods used in heat-treating Nimonic 80A, presumably the depletion of chromium in the grain-boundary region is not without its disadvantages. Can Dr. Betteridge and Mr. Franklin give any indication of the extent to which the localized chromium-depleted regions affect the oxidation-resistance of the alloy?

One comment in this paper seems a little controversial. The authors suggest that annealing of the matrix may in itself promote high creep strength, presumably by removing lattice defects. Dr. Betteridge supports this view by quoting his experiments on pure aluminium annealed at 200° C., but I, personally, would welcome any additional evidence that might be available on what at first sight seems a very unusual effect. Are we really to believe that annealing, if done well, should be a strengthening operation? If so, very few of us seem to have the knack of good annealing!

Among the materials examined by Dr. McLean and Mr. Farmer were five commercially pure metals; but, in considering the results, it seems particularly important to stress that the purest, Chempur tin and zinc, may have contained 100 p.p.m. and the iron 300 p.p.m. of impurities. Such remarks as "as little as 0.01% of impurities" suggest that these considerations are sometimes ignored. It is surely important to remember that 1 c.c. of a metal contains about  $10^{29}$  atoms; so that, even with the tin, every c.c. contained  $10^{13}$  impurity atoms. If these were distributed uniformly,

every 30th atom in the lattice would be an impurity atom; but it is quite certain that the impurities are clustered much more densely, particularly near the grain boundaries. As McLean suggests, it seems that these concentrations must be taken into account and that they may have a profound influence in hindering grain-boundary slipping in commercially pure metals, and so inducing cracking. (None of the authors, incidentally, has pointed out that commercially pure lead is particularly liable to cracking at low creep rates.) Could tests be made on some zone-refined samples of the metals used, to determine the effect of greatly reducing the impurity concentration?

Finally, I am a little puzzled as to the reasons for choosing the copper-0.37% beryllium alloy for creep testing. As far as I am aware, very little is known about the mechanism of any possible precipitation in this particular alloy. On the other hand, a good deal is known about the alloys of higher beryllium content, and by varying the temperature of precipitation of the impurity content, very wide variations in structure can be obtained. It is possible to produce either continuous precipitation or very marked discontinuous precipitation (with soft boundary zones depleted in beryllium), and it would seem that further work with, say, a 1.7% beryllium alloy, with and without added impurities, would provide some most interesting data.

Dr. McLEAN (*in reply*): I fully agree with MM. Plateau, Crussard, and Constant, and also with Dr. Heslop, that the critical stress which has to be applied if cracks are to form during creep at grain corners (type (a) in the paper) may depend upon conditions. I think the essential point is that a certain minimum stress is needed before these cracks can form. If the applied stress is less than this minimum, fracture can occur only by the alternative process, namely, the formation and development of holes (type (b) in the paper). If the applied stress is greater than this minimum, fracture can in principle take place by both processes, and will occur in practice by whichever of the two processes is faster under the given conditions. Should grain-corner cracks form faster than holes immediately the minimum stress is exceeded, then a constant critical stress will be observed over a range of temperature and strain rate.

This, I believe, is what has happened with all the alloys examined except Nimonic 80A. In Nimonic 80A, on the other hand, and in the Nimonic 90 alloys examined by Dr. Heslop, I suggest that grain-corner cracks did not form faster than holes until a stress well above the minimum was applied, giving rise to a critical stress which depended upon conditions.

It is difficult to see why the critical stress with Nimonic 90 depends on temperature according to Dr. Heslop's observations and is constant according to mine. Although it is tempting to suggest that there was some difference in the testing conditions, and indeed many factors might conceivably have some effect, it is hard to see what difference could cause the apparently large alteration observed.

I agree with MM. Plateau, Crussard, and Constant that precipitates should be capable of hindering sliding by pinning grains together, and that this ought to increase the time needed for grain-corner cracks to form. Probably a condition that has to be satisfied is that the cohesion between precipitate and matrix be high; put differently, the surface energy of the precipitate must be large. If it is small, the precipitate/matrix interface should provide easy nucleation of holes, leading to fracture by their development.

In reply to Mr. Eborall, do not the irregularities in sliding along a single grain boundary prove that obstacles along the boundary are important, as well as junctions of three grains?

I appreciate Dr. Weertman's sympathetic remarks. However, one of the largest failures of the correspondence to which he refers occurs with cadmium. Here the sliding is too large, not too small.



Dr. BETTERIDGE and Mr. FRANKLIN (*in reply*): MM. Plateau, Crussard, and Constant have queried our hypothesis of the mechanism by which intergranular precipitate of carbide prolongs the stress-rupture life of Nimonic 80A, and have made an alternative proposal. In our view the available evidence is inadequate to decide which is the better explanation of the effect on the properties, although we are satisfied that depletion in chromium does occur. Micro-probe analyses would certainly confirm this depletion, but would not determine whether the depletion or the anchoring effect of the carbide precipitate was the factor operative in prolonging the life. It is suggested that long periods of heating in the region of 1050° C. would remove chromium impoverishment by diffusion, without much effect on the precipitated carbide, and the result of such treatments (followed by suitable ageing treatments) would help to determine the nature of the mechanism.

The identity of the carbide formed at the grain boundary is a rather more complex matter than we had considered suitable for inclusion in our paper. Our examination of these carbides by extraction and X-ray-diffraction analysis has shown that on slow cooling from 1150° C. or above to around 1040° C.  $M_7C_3$  is precipitated in Nimonic 80A. Subsequent heating below 1040° C. transforms this to  $M_{23}C_6$ , the transformation being completed in less than 24 hr. at 950° C., but more slowly at lower temperatures. Thus, the transformation was incomplete after 200 hr. at 750° C. or 500 hr. at 700° C., but complete after 4000 hr. at 750° C. or 14,000 hr. at 700° C.

Dr. Chaston has provided under his heading (c) an admirable qualitative summary of the objectives in developing improved high-temperature alloys. While it is not difficult to develop alloys with increased strength of grain (resistance to creep), the provision of the necessary increase in resistance to intergranular fracture is a much more difficult problem.

The influence of chromium depletion of the grain boundaries on resistance to oxidation has not been noticeable; in a strongly oxidizing environment, in the range 600°–800° C., only a very thin oxide layer is formed, with slight penetration along the grain boundaries to the extent of a few ten-thousandths of an inch. No marked change in this characteristic has been observed with modification in heat-treatment. With Nimonic 75 (Cr 20, Ti 0.3, C 0.1%, Ni balance), however, which precipitates chromium carbide in a similar manner to Nimonic 80A, intercrystalline attack by strong pickling solutions can occur when cooling from annealing has been at an unsatisfactory rate.\*

Our suggestion that increase of the solution temperature of Nimonic 80A increases the creep-resistance by improvement of the degree of annealing of the matrix is puzzling to Dr. Chaston. We suspect that this is because he is thinking in terms of normal-temperature properties, when heavy cold work increases strength and annealing reduces it, a high density of dislocations producing strengthening by interfering with each other's freedom of movement. At high temperatures, when creep takes place at stresses below the short-time elastic limit, the reverse applies, and the lower the density of

dislocations or other lattice defects, the less the creep. Alternatively, the effect may be described in terms of increased grain-size after higher-temperature solution-treatments, but we consider that creep rate is determined more by lattice perfection than by grain-size. With conventional methods of treatment, however, the two factors may be inseparably related.

Dr. NIELD and Professor QUARRELL (*in reply*): The results of MM. Plateau, Crussard, and Constant show some interesting similarities to our own. In particular, they have shown that examples of ferrous materials can be found which exhibit behaviour similar to that observed in the aluminium alloys we studied. In the absence of any definite information, we must assume that the tests whose results are given were conducted under approximately constant rates of creep or applied strain. If this is the case, the information presented in Fig. A is very similar to that which would be obtained from our Fig. 1 (p. 482) by plotting reduction in area against temperature for a given strain rate. It is perhaps unfortunate that the term "equicohesive temperature" has been used in the past to describe some fairly definite temperature, largely independent of other variables, at which the strengths of grains and grain boundaries become equal. Our own results show that the so-called "equicohesive range" is considerably dependent upon the applied strain rate, so much so that it is probably unwise to use the term without specific mention of the strain rate.

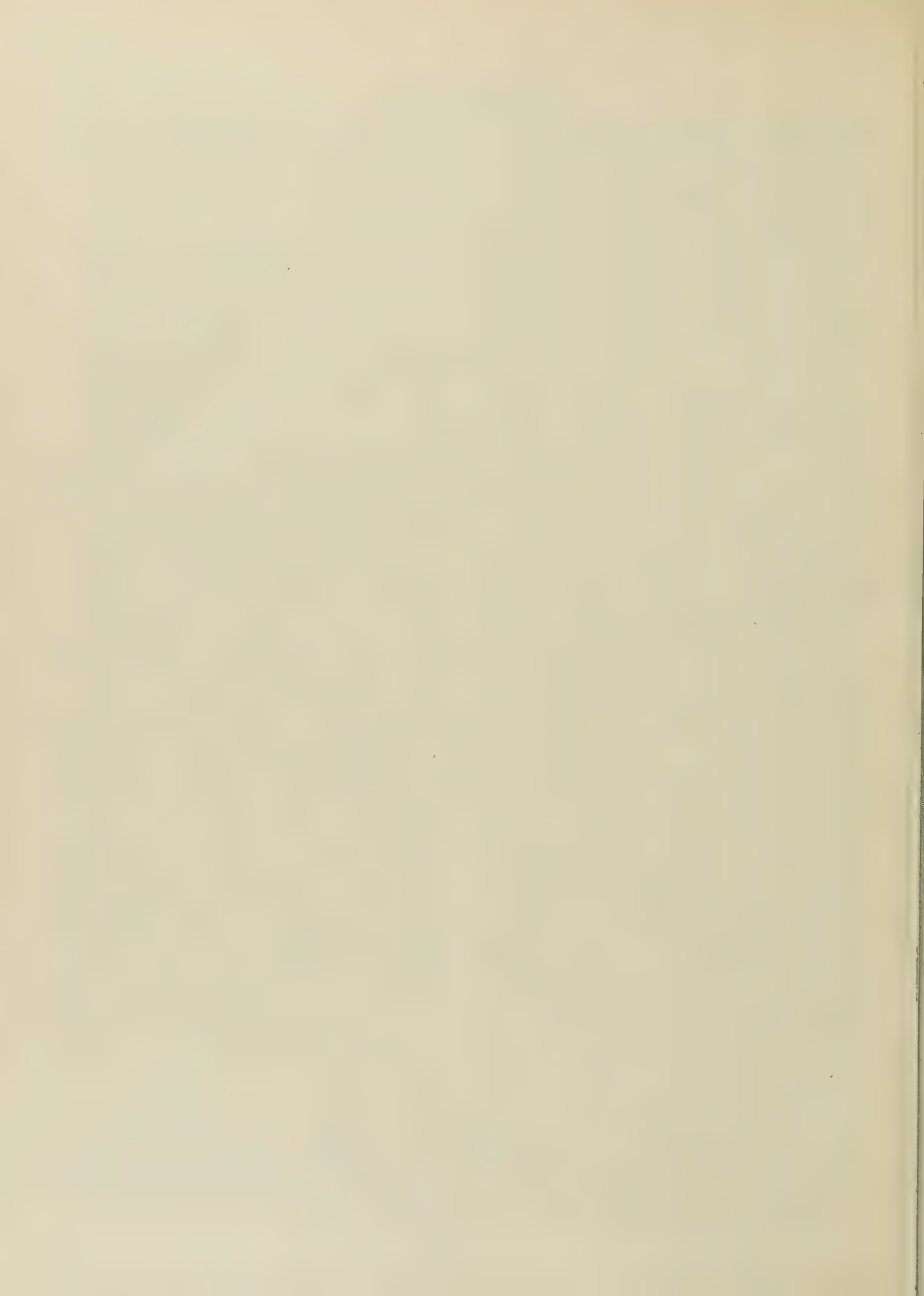
We are sorry that we have not made our proposed mechanism clear to Mr. Eborall. On re-reading the discussion in our paper, we wonder whether this is because the emphasis was placed upon crack formation instead of upon the formation of crack nuclei. It would be wrong to suggest that once such nuclei are formed they can grow only by further grain-boundary sliding. There may be other processes, including vacancy condensation, which contribute to crack growth, though we believe that grain-boundary sliding is of primary importance in the production of crack nuclei.

Although sliding is most frequently associated with oblique boundaries, it is not safe to assume that the appearance of a transverse boundary in a plane section denotes the existence of a grain-boundary surface normal to the stress axis. Considerable differences of level are frequently observed across cracks at so-called transverse boundaries, and there is no justification for assuming that sliding has not occurred on these boundaries, cf. offsetting in silver wires.†

We feel that the evidence does not justify the interpretation of an activation energy derived from the onset of boundary sliding as being the activation energy for vacancy diffusion through the lattice. We agree that the energy is probably of the correct order for this process, but we hesitate to draw such an important conclusion from such slender evidence. The experimental observations lend much greater support to the mechanism we have proposed, and the value of the activation energy is equally consistent with the mechanism of boundary self-diffusion.

\* W. Betteridge and T. E. Cound, *J. Inst. Metals*, 1954–55, **83**, 262.

† A. P. Greenough, *Phil. Mag.*, 1952, [vii], **43**, 1075.





## 1780A THE NATURE OF THE REAL CRYSTAL \*

By PROFESSOR F. C. FRANK,† O.B.E., D.Phil., F.R.S., MEMBER

## SYNOPSIS

The imperfection of real crystals has been known since 1912. In 1934 a published symposium summarized the then-existing knowledge about the subject. The same year saw the introduction of the idea of crystal dislocations, which proved to be the essential concept for a more precise description of crystal imperfection.

The present lecture traces the way in which this precision of knowledge has developed, culminating in methods of making dislocations visible, so that now in some few cases we can accurately see what the "mosaic structure" really is. Distinction has to be made between impurity-segregation substructures and disorientation substructures. The nature of both is now understood. So is the genesis of the former, but that of the latter only partially; it is discussed in detail for the case of growth from a pure melt.

## I.—INTRODUCTION

THE title of my lecture, "The Nature of the Real Crystal", formed the basis of a special issue of *Zeitschrift für Kristallographie* in 1934, in which Niggli organized a kind of symposium by correspondence about this subject. It was a very significant date in the history of crystal physics. It marked the burial of the Zwicky<sup>1</sup> theory, which was no doubt taught to many of us as students. That theory was dead already, killed by Orowan,<sup>2</sup> but Buerger<sup>3</sup> still found it necessary in that written symposium to drive a stake through its heart to stop the ghost of the theory walking. Nineteen thirty-four was the year in which Taylor<sup>4</sup> and Orowan<sup>5</sup> introduced crystal dislocations to the world, so crystal dislocations have just now come of age. Taylor<sup>6</sup> contributed an article on them to that special issue of *Zeitschrift für Kristallographie*, and it is interesting to note that for him they did not replace the mosaic structure, but were something additional. He accepted mosaic boundaries, and used them as obstacles to dislocations in his theory: he did not know exactly what they were, and for his purposes did not think it mattered very much.

Buckley,<sup>7</sup> in his article, stated in effect that he did not believe in the mosaic structure. I think it is fair to say that he was perfectly right not to believe in that version of mosaic structure which he pictured to himself and did not believe in, but that what he pictured was nothing to do with what Darwin<sup>8</sup> had shown to exist. I like to say that the lattice theory of crystal structure was produced by theoretical physics and was fully developed and generally accepted when the experiment of Friedrich, Knipping, and Laue<sup>9</sup> in 1912, intended to confirm it, showed that it was not true: the diffraction spots were in the right places but had quite the wrong intensities. As we all know, Darwin soon showed that the observed intensities would be produced if most crystals had coherent lattice patterns only over a few thousands or tens of thousands of atomic spacings, and for purposes of calculation he assumed blocks of perfect structure of this order of size, somewhat out of alignment with each other—a conglomerate structure as he called it, or a

mosaic as everybody else called it soon after. He said that he believed warping was more probable than these sharp discontinuities, and that a variety of models would produce the same observed result; but that warning was soon overlooked. With the exception of Zwicky,<sup>1</sup> who had a very definite model which was obviously wrong, I have always found it very difficult to ascertain how people pictured the mosaic structure in those days; but of one thing I am certain, that many of them had pictures in their minds which Buckley was right to disbelieve. I suppose that even those who did not accept Zwicky's reasoning were influenced by him in their imagination.

I do not think Smekal<sup>10</sup> should be accused of that. We owe him a great deal for continuously emphasizing the important distinction between structure-insensitive and structure-sensitive properties of crystals, and Smekal's *Lockerstellen* (loose places) in crystals were not a false picture. He merely resisted attempts to make him say prematurely precisely what those loose places were. The awkward question: What kind of loose place in a crystal is incapable of healing itself? can now be simply answered: It is a dislocation.

## II.—LINEAGE STRUCTURE

Crystal dislocations were introduced to the world in 1934, but so was another idea, Buerger's concept of lineage structure,<sup>11</sup> which was his main contribution to that Symposium. It was a simple idea, with evident truth in it, that if anything happens to produce warping during the growth of a crystal, and that warping is not homogeneous, then surfaces are formed within the crystal at which the lattice orientation discontinuously changes, and the resulting surface of discontinuity persists thereafter, dividing the crystal into distinct lines of descent from a common ancestry, which may in turn be further subdivided. His chosen term, "lineage", was admirably descriptive of this type of structure, and I would certainly retain it. I would use the term "macro-mosaic" in a more general sense—the subdivision of the crystal into visible portions of slightly different orienta-

\* Delivered at the Annual Spring Meeting, London, 29 March 1955.

† Professor of Physics, H. H. Wills Physical Laboratory, University of Bristol.

tion irrespective of the manner in which it has been produced. Lineage structure is one of the kinds of macromosaic.

However, there are two necessary comments to make about Buerger's original paper on lineage structure. One, which he made himself, is that for obvious reasons of simple representation his figure showing what he means by lineage is two-dimensional, and shows bending only about an axis normal to the growth direction. Three-dimensionally, rotations about other axes must also be reckoned with, and these include the growth direction itself. A progressive rotation about the growth direction in the elongated lineage cells is a twist instead of a bend, and the experimental truth of the matter, in the case of moderately pure substances growing from the melt, is that twists of this kind occur to a far larger extent than bends. I believe that the bends occur only in relatively impure melts, and with impurities that enter appreciably into solid solution.

### III.—SMIALOWSKI STRUCTURE

The second important comment on Buerger's paper<sup>11</sup> is that what he presented as his first example of a lineage structure was not that at all. He showed a single crystal of zinc, deeply etched. Anyone who has handled single crystals of metals must have observed markings of the kind visible there, and must have wondered how true was the imagined model of a perfect crystal, even when planar slip bands as seen in that photograph tended to set his mind at rest. I have no doubt that the coarse marking near the bottom of the crystal shows that there was considerable supercooling of the melt before nucleation of the crystal occurred, and that the initial growth was dendritic. With that kind of growth there is every likelihood that the thin dendrite branches will get bent, and the resulting crystal will contain perhaps severely disoriented regions, which constitute one kind of lineage structure. If one is not fussy about disorientations of 5°, this dendritic method of crystal growth may be much the quickest possible, and the conditions for crystal growth sometimes recommended in the literature produce just that result; but it is not to be recommended when any precision of orientation is desired. Buerger's next photograph showed a lightly etched cleavage surface taken from the top of the crystal, where I think we can presume the dendritic growth had ceased. It shows a hexagonaloid pattern of what Buerger calls "lineage cells"; but I do not think that is what they are.

This kind of pattern was next examined in detail in 1937 by Smialowski,<sup>12</sup> who obtained examples in zinc, copper, and lead. Smialowski showed that it was produced by impurities, and was distinct from dendritic growth. Chalmers and his co-workers have since studied it in various metals, and have explained the way in which it is produced. It is a segregation phenomenon, of a kind which can always be expected in the growth of crystals from impure melts. One part in 10<sup>4</sup> of impurity is sufficient, and there need not be anywhere near a eutectic composition. We shall come back to the subject of this segregation structure in a little while. My present purpose is to point out that there is no necessary disorientation between the cells of the Smialowski

structure. Buerger named one sort of substructure in crystals, but he illustrated two.

### IV.—THE DISLOCATION MODEL OF SUB-BOUNDARIES

The next important step was taken in 1939, when Burgers<sup>13</sup> and Bragg<sup>14</sup> pointed out that surfaces of discontinuity in the orientation of crystal lattices, such as those pictured in Buerger's original diagram of lineage structure, or that might be supposed to exist between the blocks of Darwin's mosaic, were equivalent to grids of dislocations. The picture is now a familiar one.

This picture of sub-boundaries as systems of dislocations can be approached from two sides. One may consider putting the two crystals together and estimate the positions the atoms will come to in equilibrium; alternatively, one may consider dislocations present in the crystal and exerting forces on each other. Edge dislocations draw others like them into a parallel array. A pair of crossed screw dislocations attract each other just at the crossing point, and so stabilize a crossed grid of screw dislocations.

I wonder whether the novelty of those pictures was realized at the time. Taylor had added the idea of dislocations to the mosaic structure. In the new picture introduced by Burgers and Bragg in 1939, the separate mosaic structure disappeared. It became an arrangement of dislocations.

Those pictures were just a little hard and stiff. They seemed to suggest that sub-boundaries might exist only in certain orientations. It was left to me,<sup>15</sup> after the War, to generalize the approach and show that suitable dislocation nets can describe the boundary between slightly disoriented crystals in any orientation whatsoever. For that purpose one of the most useful rules is that a number of dislocations may meet at a point when the Burgers vectors make a closed circuit of nearest-neighbour connection in the lattice. In the face-centred cubic lattice there are equilateral triangles of adjacent lattice points, and we therefore anticipate junctions of three dislocation lines at a point, meeting symmetrically, that is, at 120°.

### V.—VISIBLE DISLOCATIONS

The greatest change since those pre-war days, and one which has come about in the last five years, is that we can now see dislocations, or rather that we recognize them when we see them. The first to be recognized were those associated with crystal growth. Crystal growth gives rise to spiral terraces on crystal surfaces,<sup>16</sup> which can, in certain circumstances, be made visible. The centre of each spiral is a dislocation. The first seen were on non-metals, and served to convince the doubtful that dislocations really existed. Forty<sup>17, 18</sup> managed to see them on sublimed crystals of silver and some other metals by a fortunate tarnish localized along the monoatomic steps in the surface. A point of interest in these specimens was that the number of dislocations was few—four or five, for example, on an area of a few hundredths of a square centimetre. These sublimed crystals were



much more perfect than metal specimens usually are. This helps to dispel the idea that there is a fundamental limit to the possible perfection of crystals.

It is also possible to make the ends of dislocations visible by etch pits. Lacombe<sup>19</sup> discovered this, but it was left to Shockley and Read<sup>20</sup> to point out that that is what they were. As a matter of fact, the truth is more complicated. The etch pits, in that case, mark precipitate particles, but the precipitate particles form only on dislocations. The phenomenon noted by Lacombe was not different in principle from the "veining" observed in other metals, and attributed (by Northcott<sup>21</sup> in 1932) to precipitation at sub-boundaries. The essential point brought out by Shockley and Read was that regular spacing of etch pits in the sub-boundary corresponded to a regular spacing of dislocations which would give the correct disorientation across it.

This sort of picture began to give us a clear idea of the state of imperfection of a typical metal, with some dislocations gathered into surface arrays, and others in disarray between them. But the most striking way of seeing dislocations was already in existence, though we did not know it. That is, to precipitate particles on to the dislocation lines in the interior of transparent crystals. The method goes back to Rexer,<sup>22</sup> one of Smekal's team, in 1932.

Rexer diffused sodium metal into sodium chloride crystals and cooled them slowly enough for the sodium to precipitate as fine particles in the interior of the crystal. They did not precipitate homogeneously, but there were places of dense precipitation revealing a substructure within the crystals, and especially in the neighbourhood of slip bands in crystals which had been deformed. If he had used a higher magnification, he would have been able to see the individual dislocations in those specimens. In fact, it was left to Hedges and Mitchell<sup>23</sup> to be the first to see them by this method. Their material was silver bromide, and the precipitating metal was silver, formed beneath the crystal surface by exposure to light. Their crystals were annealed, after being deformed a few per cent. in cooling after preparation by adhesion to the glass plates between which they were grown. The microscope showed that the silver precipitated on fine lines in the crystal interior, having the regular habit of meeting three at a point (as expected for dislocations in this crystal structure). In part they formed complex three-dimensional networks, but more especially they were grouped together in surface arrays, sometimes simply of parallel lines, corresponding to the dislocation model of a "tilt boundary"; sometimes they were in various forms of an hexagonal network, corresponding to the expected dislocation arrangement, in this crystal structure, for "twist boundaries", or for boundaries with some arbitrary axis of relative rotation of the two crystal regions across the boundary. In these boundaries the dislocation spacing was typically half a micron or so (corresponding to disorientations of a few minutes), and the boundaries divided the crystal up into cells of irregular shape, with typical dimensions of the order of 10  $\mu$ . Hedges and Mitchell were seeing the mosaic structure, thus verifying for the first time by direct observation that it could be a quite accurate description of the state of a crystal, and seeing its nature in quantitative detail. Nevertheless, the mosaic model was also found not to give a complete description. There

were always a few "disorganized" dislocations within the mosaic cells; and, depending on the state of anneal, there might be no recognizable mosaic cells or boundaries at all—the dislocations could form an essentially three-dimensional network, for which the mosaic description could be used only in a forced and arbitrary way, by saying that there was only one dislocation to each mosaic boundary. In terms of dislocations we can describe the whole range of these states of imperfection of the crystal, including both those to which the term mosaic is apt, and those to which it is not. With further annealing, the less-organized arrangements of dislocations tend to become more organized. The forces of interaction gather them together into surface arrays. The structure becomes more mosaic.

Let us turn now to the question of why crystals regularly contain these imperfections. It is a question still answered in only a fragmentary way, but I believe there are enough partial answers now available to say that we very likely have all the necessary principles at hand; that the problem requires only the fuller working out of ideas already thought of; and that these need only be the generally accepted ideas. I mean by this in particular that I do not think we have to follow Born<sup>24</sup> in his surmise that the almost universal imperfection of crystals must be attributed to a fundamental principle yet to be discovered, or at any rate yet to be established, which makes lattices unstable if they extend beyond a certain distance. All that Born has actually shown in this connection is that existing methods of calculating lattice properties, due largely to himself, prove somewhat faulty if the lattice extends beyond a certain distance. That is a very different conclusion, and I know of no grounds to suppose that there is more to it than that.

Metal crystals, in which the metallurgist is chiefly interested, have mostly grown either from the solid or the melt. Often they are crystals which have been annealed after some straining process, and I do not refer only to the "strain-anneal" method of obtaining single crystals or large-grained specimens. The strain certainly leaves the material full of dislocations, obtained by a great multiplication of the dislocations previously present. We have already seen how, in that part of the annealing process called "recovery", the dislocations gather into surface arrays, gradually developing a true mosaic structure. I do not doubt that what we see in the transparent crystals gives us a fairly accurate picture of what happens in metals. The further stages of this process are a slower union of the surface arrays and a gradual coarsening of the mosaic structure not very different from grain growth in a polycrystalline metal; and as in that case, too, I suppose that what prevents the process going to completion, making a perfect crystal as grain growth might make a single crystal, is the anchoring effect of impurities. In both cases the forces available for breaking away from the obstacles can be described as a product of surface tension and curvature, and the curvature diminishes inversely with the scale of the substructure. I believe that the notorious figure of  $10^8$  dislocations/cm.<sup>2</sup> in the annealed metal, which for one thing is not very accurate—it is rather the imprecision of most methods of estimating this number which allows one always to quote the *same* figure within the experimental or theoretical uncertainty—reflects only the present limits of purity in a nominally pure metal.



We have seen in Forty's sublimed silver crystals that the number can be much smaller.

When the annealing process is not one of recovery, but of solid recrystallization, we shall not generally expect the dislocations of a consumed grain to survive in the new grain. I do not think this can be totally excluded. In the case of twins we certainly expect some of the dislocations to pass continuously across the boundary. The facts regarding recrystallization in a metal with a pronounced orientation texture show that there are a number of other special orientation relationships, in addition to twinning, which produce special conditions of atomic fit at the boundary. It is a matter for consideration whether the growing crystal may develop dislocations meeting the dislocations of the crystal being consumed, to preserve this special atomic fit. I confess, though, that I am speculating in the dark. I think it is highly desirable that one of the techniques for revealing dislocations in transparent crystal should be applied to discover the dislocation structure resulting from grain growth, and particularly, if a good example can be found, from giant grain growth produced by the strain-anneal method.

## VI.—GROWTH FROM THE MELT

That brings me to the case of growth from the melt. We have already described its empirical features, the two distinct kinds of sub-structure which Buerger tended to confuse: one of them, which I call the Smialowski structure, is essentially connected with the presence of impurity, and the other is a disorientation substructure that continues to occur in the purest materials we know, which I would call the lineage structure proper. In the usual range of growth speeds for the production of single crystals from the melt, the first produces a pattern on a scale of the order of 0.1 mm., while the easily distinguishable disorientation sub-boundaries are separated by distances of an order ten times as large. They interact in a special way, but let me first consider the Smialowski structure by itself.

### 1. SMIALOWSKI STRUCTURE

Smialowski<sup>12</sup> in 1937 showed that the pattern commenced fairly abruptly after a period of growth free from it; the purer the metal, the later the substructure appeared, and so he attributed it to a special mode of segregation of impurities. He further demonstrated that the hexagonal pattern was not in a simple crystallographic orientation, but that crystallographic-orientation effects could occur. In particular, if the growth axis in zinc was near to the basal plane, the pattern at the growth surface changed from the honeycomb pattern to one of parallel furrows, and the resulting three-dimensional substructure in the completed crystal changed from one of long hexagonal cells like a bundle of pencils to one of laminæ. The lamination was not on a crystallographic plane—it might be 20° away from the basal plane of the crystal. The plane of the lamination formed the locus of a line in the solid/liquid interface which was the intersection of the basal plane with that interface. The thickness either of the laminations or the pencils in this kind of substructure is of the order of magnitude of 0.1 mm.

These conclusions of Smialowski have been confirmed and extended by Chalmers and his co-workers, and Rutter and Chalmers<sup>25</sup> have explained how they arise. In brief, the growing crystal expels impurities, and so accumulates a thin layer of concentrated impurity solution in the liquid ahead of it. If there is not much stirring in the liquid, the distribution of impurity in the layer is exponential, as  $\exp(-x/\delta)$ , and  $\delta$ , the effective thickness of the layer, is given by:

$$\delta = D/u,$$

where  $D$  is the diffusivity of solute and  $u$  the rate of advance of the solidification front. When  $D$  is  $10^{-5}$  cm.<sup>2</sup>/sec. and  $u$  is  $10^{-3}$  cm./sec., i.e.,  $1\frac{1}{2}$  in./hr,  $\delta$  is  $10^{-2}$  cm. or 0.1 mm. The impurity concentration in this layer depresses the melting point, and now if that depression is sufficient, a smooth freezing front suddenly becomes unstable. Hitherto, growing in a temperature gradient corresponding to a flow of heat from the liquid to the solid, any protrusion of the solid reached into a place of higher temperature and melted back, preserving the smooth interface. But now it reaches through the layer of increased impurity content and depressed liquidus temperature into purer liquid where the melting point is higher again. Thus, irregularities of the interface persist. The critical condition for this to happen is that the melting-point depression due to the accumulated impurity, divided by the distance  $\delta$ , should be greater than the applied temperature gradient. This is the conclusion of Chalmers. A detailed solution of the equations of diffusion and heat conduction adds only two points to it. First, for the temperature gradient we must take not the temperature gradient in the liquid but a weighted mean temperature gradient in liquid and solid, weighted with their thermal conductivities. Secondly, there is a maximum wave-length for the possible corrugations of the interface which becomes greater as the instability of the smooth interface increases, but is always of the same order of magnitude as  $\delta$ , that is typically  $10^{-2}$  cm. When we bring into consideration the surface tension of the solid/liquid interface, we find that that makes another critical condition, cutting out the corrugations of short wave-length, usually those shorter than about  $10^{-3}$  cm. Hence, a Fourier analysis of the profile of the growing solid under these conditions must be made up of components with wave-lengths in a narrow range. This does not tell us the pattern, but it does tell us its scale, essentially of the order of 0.1 mm. as observed.

The consequence of this corrugation of the interface, which may be observed by tipping out the liquid, is a correspondingly patterned distribution of impurity in the solid. This has been confirmed by Rutter and Chalmers by autoradiography, using radioactive antimony in lead. It is important to notice that this is not lineage structure in Buerger's original sense, because there is no necessary disorientation between the cells of the Smialowski substructure.

### 2. THE RELATIONSHIP BETWEEN SMIALOWSKI SUB-STRUCTURE AND LINEAGE

The relationship between Smialowski substructure and disorientation substructure, or lineage, has been clarified by the work of Hulme.<sup>26</sup> That the two structures were distinct followed from the work of the Chalmers group,



showing that they differed in scale. Hulme, working with zinc, used Berg-Barrett X-ray imaging to reveal lattice disorientations in the same surfaces as those at which he had rendered the Smialowski structure visible by imperfect electropolishing (working near the bottom of the polishing range of current density). This showed that the disorientation sub-boundaries do not visibly affect the pattern of Smialowski cells, but the latter exert a strong influence on the disorientation sub-boundaries. These preferentially follow the Smialowski boundaries, like cracks preferentially running in the mortar of a disintegrating brick wall. Occasionally they cross a cell, as cracks will occasionally cross a brick. Optical examination of the surface reveals only the Smialowski structure. The X-ray image, on the other hand, shows both the disorientation boundaries and the boundaries between Smialowski cells with no detectable disorientation. The visibility of these boundaries in the latter case can be attributed to a change in extinction consequent on the impurity content. This could be produced in various ways. It is quite likely that there are dislocations associated with these impurity walls when there is no net disorientation, though we cannot be sure of this. The lineage boundaries must have an independent origin, but suffer a small-scale distortion in the presence of Smialowski structure through attraction of their dislocations to impurity-rich regions.

### 3. LINEAGE STRUCTURE

Now we have to explain the production of the dislocations which constitute the lineage structure. The really striking fact about it is the direction of the disorientation, which is consistently a rotation about the growth axis, the axis of the temperature gradient; each of the elongated individual cells of the lineage is twisted to begin with, settling down into an approximately constant orientation apparently, anything from a few minutes to a few degrees out of parallelism with its neighbours. This rotation about the growth axis is a very general result, demonstrated by Chalmers in a number of metals; it first came to my notice in some artificial rock-salt. That signifies that the sub-boundaries of the lineage structure are composed of edge dislocations parallel to the growth axis. The only theory in the field is due to Teghtsoonian,<sup>27</sup> a co-worker of Chalmers. He has not presented it in great detail, and I do not know whether my version will be identical with his or not, but in any case his is the basic idea. It attributes the substructure to the condensation of vacancies present in the metal just below its melting point. We can assume an equilibrium concentration of them in the newly formed metal, say, in order of magnitude, one in  $10^5$  lattice sites. As the metal cools the equilibrium concentration falls, as  $\exp(-U/kT)$  where  $U$  is the energy of vacancy formation. The existing concentration is then highly supersaturated. If dislocations are present, they condense on to these, causing them to climb. If there are not enough places on which they can condense, then they will aggregate among themselves, just as the atoms in a supersaturated vapour do, and according to much the same quantitative laws. But, unlike the atoms in the vapour, they have two possible ways of condensing, one into compact aggregates, which are pores, and the other into flat aggregates, which become loops of edge dislocation. We

do not know the relative proportions of these two modes of condensation. If it turns out that direct condensation into flat aggregates is rare, we shall have to assume that dislocations in the seed crystal serve as initial places of condensation, and are multiplied by Frank-Read<sup>28</sup> sources acting "in climb". It does not matter if some pores also form, since they should ultimately re-evaporate, depositing their vacancies on the dislocations.

The first loops of dislocation formed in this way will be in various planes, but those parallel to the growth front will be left behind, while those edge on to it can extend by continual addition of vacancies, following up the growth front. We shall presently have a number of hair-pin-shaped loops of edge dislocation continually extending parallel to the growth axis. According to the usual laws of dislocation interaction, we shall expect them to form up into parallel grids as in Fig. 1. Each such set of  $n$

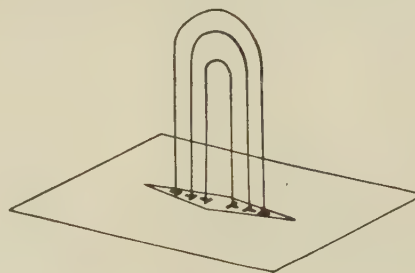


FIG. 1.

hair-pins in its growth removes all the lattice sites from a narrow rhombus  $n$  lattice spacings wide at the widest part. Now if we ask how such rhombi can be removed from the material, and the gaps closed up, without producing any extensive stresses, we arrive at the arrangement of Fig. 2, a cross-section normal to the growth axis.

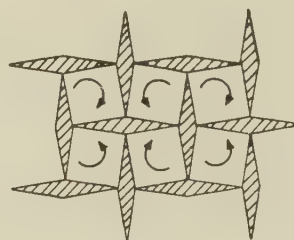


FIG. 2.

Apart from being too regular, it describes essentially what is observed.

Now let us see if this model is quantitatively acceptable. In Fig. 2 there is one rhombus for every square, and the relative area of the rhombi to the squares is just equal to  $\theta$ , the acute angle of a rhombus; that is, to the disorientation between neighbouring squares when they close up the gap. This relative area should equal the proportion of vacancies at the melting point, about  $10^{-5}$ , so we seem to arrive at an angle of  $10^{-5}$ , i.e. a few seconds instead of a degree or so. We ought to have expected this, because the hair-pin system which is just sufficient to absorb the vacancies (Fig. 3 (a)) is unstable; its upper loops are attracted to the boundary of the solid, but all the length of dislocation line which breaks out of the surface (Fig. 3 (b)) ceases to be available to absorb

vacancies. The excess of vacancies will push the dislocation sideways, leaving a central region under stress and so making it the best region for further dislocation loops to form in. These in turn will break out, and become less effective absorbers of vacancies, and so the angle  $\theta$  will progressively increase, as Chalmers observes it to do. I shall not attempt to calculate why the increase ceases at  $2^\circ$  or so.

The other important parameter defining the lineage is the diameter of the cells, observed to be of the order of 1 mm. This distance should be such that the diffusing vacancies all have a chance to reach the sub-boundaries before the temperature falls far enough to produce a high degree of supersaturation. In a temperature gradient

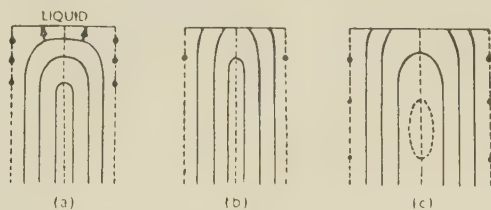


FIG. 3.

$(dT/dx)$ , the equilibrium-vacancy concentration falls by a factor  $e = 2.718$  in a distance  $kT^2/U(dT/dx)$ , i.e. in a time  $kT^2/vU(dT/dx)$ , where  $v$  is the crystal-growth rate. The distance over which vacancies can effectively diffuse in this time is:

$$l = (Dt)^{\frac{1}{2}} = \left( \frac{D_{\text{vac}} \cdot kT^2}{vU(dT/dx)} \right)^{\frac{1}{2}} \sim \left( \frac{10^{-5} \text{ cm}^2/\text{sec.}}{v} \right)^{\frac{1}{2}} \sim 1 \text{ mm.}$$

if we put as reasonable figures  $D_{\text{vac}}$  (the diffusion coefficient for vacancies)  $= 10^{-6} \text{ cm}^2/\text{sec.}$ ,  $U/kT \sim 10$ ,  $T/(dT/dx) \sim 100 \text{ cm}$ , and  $v = 10^{-3} \text{ cm./sec.}$  This is a satisfactory order of magnitude.

I think I should mention a consideration due to LeClaire,<sup>29</sup> who has pointed out that vacancies in a temperature gradient will have a thermal-diffusion drift. This drift velocity is  $D_{\text{vac}}Q(dT/dx)/kT^2$ , where  $Q$ , strictly the heat of transport, is approximately the activation energy for diffusion. This velocity is of the order of magnitude of  $10^{-6} \text{ cm./sec.}$  (1 in./month), so that this tendency for vacancies to follow the growth front may be neglected except in the case of exceedingly slow crystal growth.

If this is the correct account of the origin of lineage structure—and I see no other which will explain the observed facts—then the condensation of vacancies is a process which can importantly modify the dislocation arrangement in a material, and give rise to new dislocations if it starts with relatively high perfection, on cooling from any heat-treatment.

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